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BUREAU OF MINES

UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 9234

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Manuel J. Lujan, Jr., Secretary

BUREAU OF MINES
T S Ary, Director

Library of Congress Cataloging in Publication Data:

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Btu	British thermal unit	mg	milligram
°C	degree Celsius	mg/m^3	milligram per cubic meter
cm	centimeter	min	minute
deg	degree	mm	millimeter
dyn/cm	dyne per centimeter	pct	percent
g	gram	s	second
g^2	gram squared	wt pct	weight percent
g/cm^3	gram per cubic centimeter		

CAPILLARY WETTING RESPONSE OF COAL AFTER EXPOSURE TO AMBIENT AIR ATMOSPHERE

By H. W. Kilau[1] and J. E. Pahlman[2]

ABSTRACT

The U.S. Bureau of Mines examined the wettability of bituminous and subbituminous coals before and after exposure to ambient air atmosphere, as part of an ongoing project investigating the coal-wetting abilities of surfactant solutions intended for the suppression of dust during coal mining operations. Exposure periods were generally 7 days or less, and the changes in wetting response were measured with a capillary penetration apparatus.

Wetting solutions tested included a nonionic surfactant, two anionic surfactants, and pure distilled water. After exposure, higher ranked bituminous coals treated with nonionic surfactant solution and pure water showed increased wettability, but lower ranked subbituminous coals showed decreased wettability. With the anionic surfactants, the coals demonstrated opposite responses.

The wettability changes appeared to be related to the coal moisture content. These changes may be amplified by specific, but incompletely understood, interactions between surfactant polar groups, absorbed water, and the coal surface.

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INTRODUCTION

Coal dust arising from mining creates health and safety problems. Pneumoconiosis (black lung disease) is a serious problem frequently afflicting coal miners exposed to respirable coal dust for long periods. Also, coal dust suspended in the underground mine atmosphere constitutes an explosion and a fire hazard. In the case of methane ignition, suspended coal dust can help propagate fire rapidly throughout a mine to entrap miners before they have a chance to escape. Current Federal legislation limits coal mine atmospheres to a maximum of 2.0 mg/m³ of respirable coal dust, or lower if the dust contains >5 pct silica. Mine operators use various methods to control dust levels, including water sprays directed at the face and bits during coal cutting. However, for many mining operations, particularly longwall sections, water sprays and other conventional methods are inadequate to reduce levels below the standard threshold limit (1).³

Surfactant addition to the water used in sprays has been suggested and used in some mines for improving the effectiveness of water sprays. Surfactant addition generally helps the wetting of coal, since the coal surface is normally very hydrophobic in nature. Because of this improved wetting action with surfactant, one would predict that using surfactants in water sprays would improve coal dust suppression. However, actual experience in mines using surfactants has not been consistently positive, and improvements in coal dust suppression have frequently been below expectations. Even laboratory testing of surfactant wetting agents has shown numerous inconsistencies among various surfactant products applied to different coals and a lack of correlation with field testing.

As part of its program to reduce the exposure of mining personnel to respirable coal dust, the Bureau of Mines is investigating the fundamentals of coal wetting. A basic understanding of the wetting mechanisms is needed to properly evaluate the dust suppression effectiveness of surfactants and to achieve the potential that these reagents appear to offer for reducing coal dust levels in the underground mining environment.

One of the fundamental parameters suspected of causing problems in evaluating surfactant wetting effectiveness is the change in surface characteristics that can occur between collection of coal samples and time of wettability testing in the laboratory. The work reported here investigates this parameter by measuring the wettability of some coal samples collected and prepared under protective atmosphere and after various periods of exposure to ambient air atmospheres.

The wettabilities of the coals before and after exposure were determined with a capillary penetration method developed at the Bureau's Twin Cities Research Center (TCRC). In this method, the weight of wetting solution absorbed into a porous column of coal particles by capillary action is measured. The test is derived from the capillary rise method used by many to measure wettability of powders (2-4).

In the capillary rise method, a glass tube is filled with powdered coal that is contained by a glass-fiber filter glued to the bottom of the tube. The filter is contacted with the surface of the liquid to be tested, and the liquid front is observed for a measured time interval as it rises through the capillary volume between the coal particles. Washburn (2) derived an expression for this liquid penetration, equating the powder column to a bundle of capillaries.

$$h^2 = \frac{kr\gamma \cos \theta}{2\eta} \cdot t, \qquad (1)$$

where h = rise height of liquid front, cm,

   r = mean radius of capillaries, cm,

   γ = surface tension of liquid, dyn/cm,

   θ = contact angle, deg,

   η = viscosity of liquid, poise,

and t = time, s.

The mean radius is modified with the constant term k to allow for the tortuous path through the capillaries and is dependent on the size and packing of the powder (5). Alternatively, the tube of coal can be withdrawn from the liquid after the time interval and weighed to determine the liquid uptake. This alternative method is superior because the liquid front visible at the glass wall sometimes does not accurately reflect the interior progress of the front. The weight gain measured can be related to the rise height, h, of the Washburn equation if a knowledge of coal-column geometry, porosity, and liquid density are available.

$$W = \frac{hP\rho\pi R^2}{100} \qquad (2)$$

where W = weight gain, g,

   ρ = density of wetting solution, g/cm³,

   P = porosity of packed column of powder, pct,

and R = inner radius of containing tube, cm.

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³Italic numbers in parentheses refer to items in the list of references at the end of this report.

The Washburn equation can then be expressed in terms of weight gain for a given coal column and wetting solution as

$$W^2 = At, \qquad (3)$$

where

$$A = \left(\frac{P\rho\pi R^2}{100}\right)^2 \frac{kr\gamma \cos\theta}{2\eta}. \qquad (4)$$

Murata and Naka (6) attempted to continuously observe liquid uptake by suspending the tube of coal from a sensitive electrobalance while the filter and tube were directly in contact with the liquid. However, the authors of the present Bureau work found that surface tension and buoyancy effects drastically interfered with the recording of the weight gains in this arrangement. In the capillary penetration test devised for this work, surface tension and buoyancy interferences were almost entirely eliminated by using a wicking system to bridge the troublesome interface between the coal surface and bulk liquid.

EXPERIMENTAL PROCEDURE

In this investigation, 11 coal samples were tested (6 bituminous and 5 subbituminous). Chemical analyses for the coals, as described by the supplier, are given in table 1.

All of the coals were obtained from Pennsylvania State University's premium coal bank.[4] These samples were collected and prepared by the supplier with special precautions to avoid oxidation. The samples were sealed immediately under inert (argon) gas when collected at the minesite, and all subsequent handling and crushing operations were carried out in protective argon atmospheres. The coal samples were received from the supplier in sealed cans and were either minus 20- or minus 60-mesh size. Preparation for wettability testing required further

grinding to minus 200 mesh (except sample 7, which was ground to minus 100 mesh). This final grinding was performed with a mortar and pestle in a glove box purged with argon gas. Thus, the coal surfaces should have been free from alterations caused by exposure to ambient air atmospheres and resembled coal that is freshly cut at the face during an underground mining operation.

The wettabilities of the minus 200-mesh coals were tested immediately after the coals were removed from the glove box and were retested following various periods of exposure to the ambient atmosphere of the laboratory. The fine coal was exposed by spreading the sample on a large watch glass in a layer <2 mm thick. The exposed coal was sampled for wettability testing at various periods up to 8 days, but usually the coal was sampled after 3 and 7 days. The environment of the laboratory was not unusual. The coals were not exposed to chemical fumes.

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[4]Penn State Office of Coal Research (PSOC).

Table 1.—Chemical analyses of bituminous and subbituminous coal samples used in wettability experiments, as received, weight percent

Sample	Coal seam and location	Rank[1,2]	Moisture	VM	Ash	Carbon Fixed[3]	Carbon Total	Hydrogen[4]	Nitrogen	Total sulfur	Oxygen[5]
1 ...	Upper Freeport, PA ...	mvb	2.0	25.8	12.7	59.5	74.1	4.4	1.5	2.1	3.2
2 ...	Colorado B, CO	hvAb	1.8	37.7	7.2	53.4	74.8	5.0	1.6	.6	9.0
3 ...	Upper Freeport, PA ...	hvAb	2.9	36.2	8.5	52.4	73.3	5.2	1.7	2.0	6.4
4 ...	Fort Scott, OK	hvAb	3.5	39.4	10.0	47.1	70.8	5.0	1.6	4.7	4.4
5 ...	Weir-Pittsburgh, MO ..	hvAb	6.3	37.2	16.8	39.8	60.3	4.4	1.4	9.6	1.3
6 ...	Bevier-Wheeler, MO ...	hvBb	9.3	34.8	18.6	37.4	56.3	4.1	1.1	5.8	4.9
7[6]...	Colorado Q, CO	subA	13.0	34.2	5.7	47.1	61.1	4.1	1.6	.3	14.1
8 ...	Colorado I, CO	subA	16.6	26.2	5.8	51.5	59.3	4.2	1.6	.5	12.0
9 ...	Anderson, WY	subB	17.8	37.8	8.6	35.8	53.0	3.4	.9	1.0	15.5
10 ...	Upper Wyodak, WY ...	subB	19.8	38.2	7.2	34.8	54.4	4.0	1.0	1.5	12.2
11 ...	McKay, MT	subB	23.1	28.5	7.5	40.9	51.2	3.1	.8	1.7	12.5

VM   Volatile matter.
[1]mvb   Medium-volatile bituminous.
hvAb High-volatile A bituminous.
hvBb High-volatile B bituminous.
subA Subbituminous A.
subB Subbituminous B.

[2]Designated by supplier.
[3]By subtraction [100 - (pct moisture, VM, ash)].
[4]Excludes moisture.
[5]By subtraction [100 - (pct moisture, ash, carbon, hydrogen, nitrogen, sulfur)].
[6]Minus 100 mesh.

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The experiments were run in the summer, but the room where the coal was exposed was air-conditioned during the workday. Therefore, the exposure of the coal is believed to have been principally confined to oxygen, nitrogen, and moisture from the ambient air atmosphere.

Three surfactants were used in the wetting experiments: Two were anionic (forming negative anions when dissolved in water), and the third was nonionic. One of the anionic surfactants used was a 75-wt-pct solution of sodium di(2-ethylhexyl) sulfosuccinate (SD2ES) dissolved in alcohol and water. This surfactant solution was obtained as the commercial product Aerosol OT-75,[5] manufactured by American Cyanamid Co. The other anionic surfactant was also obtained from American Cyanamid, as their product Aerosol MA-80, which is described as an 80-pct solution of the compound sodium dihexyl sulfosuccinate (SDHS) dissolved in alcohol and water. The nonionic surfactant used was an ethoxylated acetylenic glycol (EAG) compound, formulated by Air Products and Chemical Corp. Specifically, the manufacturer describes this surfactant product as 2, 4, 7, 9-tetramethyl-5-decyn-4, 7-diol with 65-wt-pct ethylene oxide adduct. The product is sold under the name Surfynol 465. (These surfactants were chosen for the exposure tests because they had demonstrated excellent capability for wetting coal in earlier Bureau survey testing when applied as dilute (<1.0 pct) aqueous solutions to coals that were poorly wettable in pure water.) The pure water used to prepare the surfactant wetting solutions, as well as for use in the high-purity water wetting tests, was first distilled and then passed through a deionizer cartridge.

The wettabilities of the coals in pure water and the dilute surfactant solutions before and after various exposure times were measured with the capillary penetration test. A diagram of the capillary penetration apparatus is presented in figure 1, and the wicking system is detailed in figure 2. The electrobalance used to continuously record the weight gain of wetting solution imbibed into the coal column had a calibrated range of 0 to 30 g and a sensitivity of 0.003 mg. Whatman glass filter pads (grade GF/0, 1.0-cm diameter) were glued to plastic tubes (cut from 0.8-cm-ID pipettes) with rubber cement. The wick system consisted of two strands of dental floss (Johnson's extra-fine, unwaxed) threaded through a nonwettable, plastic capillary tube to contact the filter pad. In operation, 0.5 g of coal particles was loaded into the tube and settled with light tapping, and the wick and capillary tube were inserted in the wetting solution to a depth of 4 mm. The initial weight gain resulting from rapid liquid uptake onto the wick and filter disk was recorded, as well as the later stage of slow penetration into the coal. The intersection of lines drawn tangent to the weight-gain curves of these two stages was designated as "zero time" for initial penetration of surfactant solution into the coal column. Figure 3 illustrates the technique for two typical weight-gain curves. Region 1 on the curves derives from the initial, rapid imbibition of liquid into the wick and filter disk only, while region 2 is a transition region in which imbibition likely is occurring in both the filter disk and coal column simultaneously, the filter disk nearing saturation and the coal beginning to imbibe. In region 3, liquid is being imbibed exclusively into the coal column at a slow rate. For curve A in figure 3, the zero time for initial imbibition into the coal column is easily established since simultaneous imbibition by filter and coal is nearly

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[5]Reference to specific products does not imply endorsement by the Bureau of Mines.
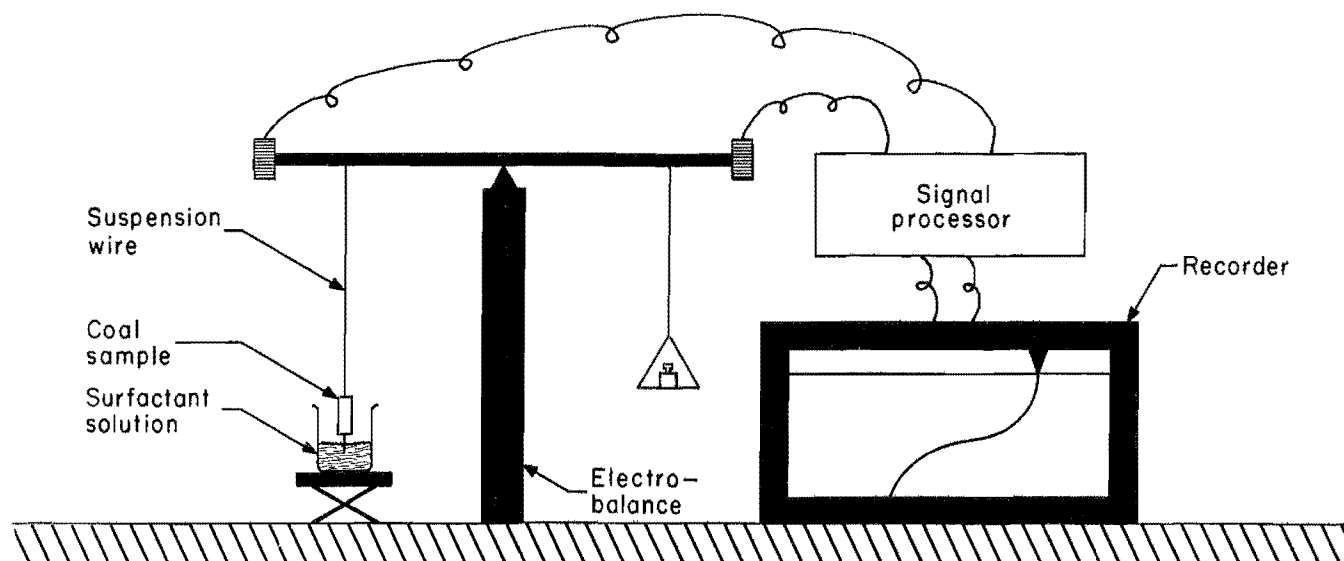

Figure 1.—Schematic of capillary penetration wetting test apparatus.

Figure 2.—Schematic of wicking system used in capillary penetration wetting test.

Figure 3.—Method for establishing zero time for penetration of liquid into coal column used in capillary penetration wetting test.
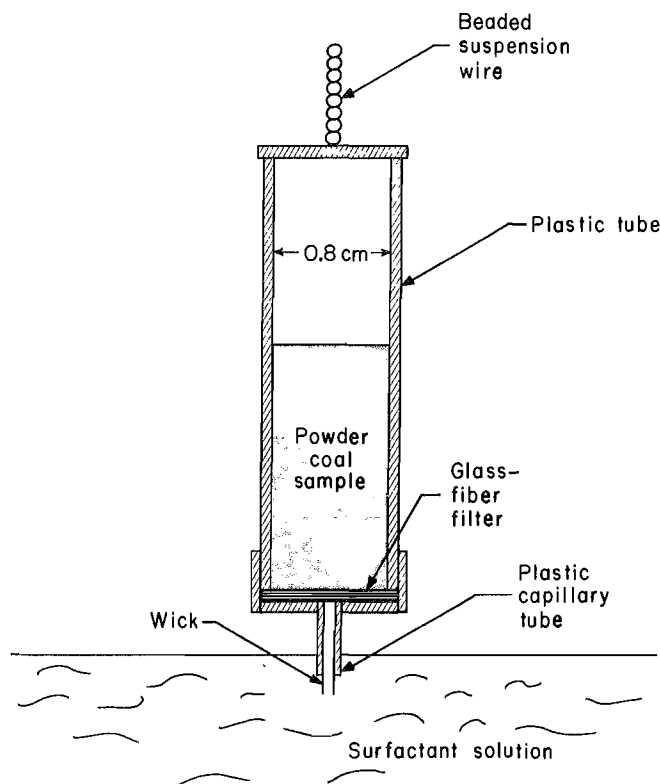
absent and the rates of liquid imbibition are very different and clearly distinguishable for the filter and the coal. However, frequently, simultaneous imbibition occurs to a pronounced degree, and zero time becomes ill-defined in region 2 (fig. 3, curve B). To determine zero time for wetting of the coal column, lines are drawn tangent to the weight-gain curves in the regions of approximately constant slope of each of the two stages. The two tangents are extended until they intersect to mark the zero time. Essentially, this intersection probably represents the zero point for the ideal case in which imbibition into the coal column would not begin until the filter and wick were completely saturated with wetting solution.

The tangent method described provides a means of establishing a consistent zero time as long as the rates of liquid uptake in filter and powder column are different and clearly distinguishable, which was the case for all the coals

examined in this report. It is to be emphasized that the weight gains plotted in all the figures of this report include only the weight increase occurring after the zero time established by the tangent intersection method described above. The duration of a test was generally about 30 min, and all tests were performed at ambient room temperature. At least two or more tests were run for each experimental condition (i.e., coal sample, surfactant type and concentration, and exposure time). For each experimental condition, a curve was selected for presentation in each of figures 4 through 9 as most representative of the whole, but it was not, strictly speaking, an average curve. Computed average curves were not considered advisable because of variable periods of arrest or semiarrest in the weight-gain curves. The averaging of data points from each individual curve to construct an average curve yields a curve that is misleading and nonrepresentative. Surface tensions of all the wetting solutions at 29° C were measured using a du Nouy ring-type instrument.

EXPERIMENTAL RESULTS

Capillary penetration tests before and after exposure to ambient air atmosphere in the laboratory were performed on the 11 coal samples (table 1) using high-purity water as the wetting solution. The wetting results for each coal before and after exposure are presented in figures 4 and 5 as Washburn plots (time versus the square of the weight

gain, equation 3). The resulting curves usually exhibited either two- or three-stage wetting behavior. In the two-stage wetting process, a rapid initial imbition of liquid occurred within the first 100 s, followed by a second stage (usually linear) extending to the termination of the experiment (particularly noticeable in figure 4A, curves A and
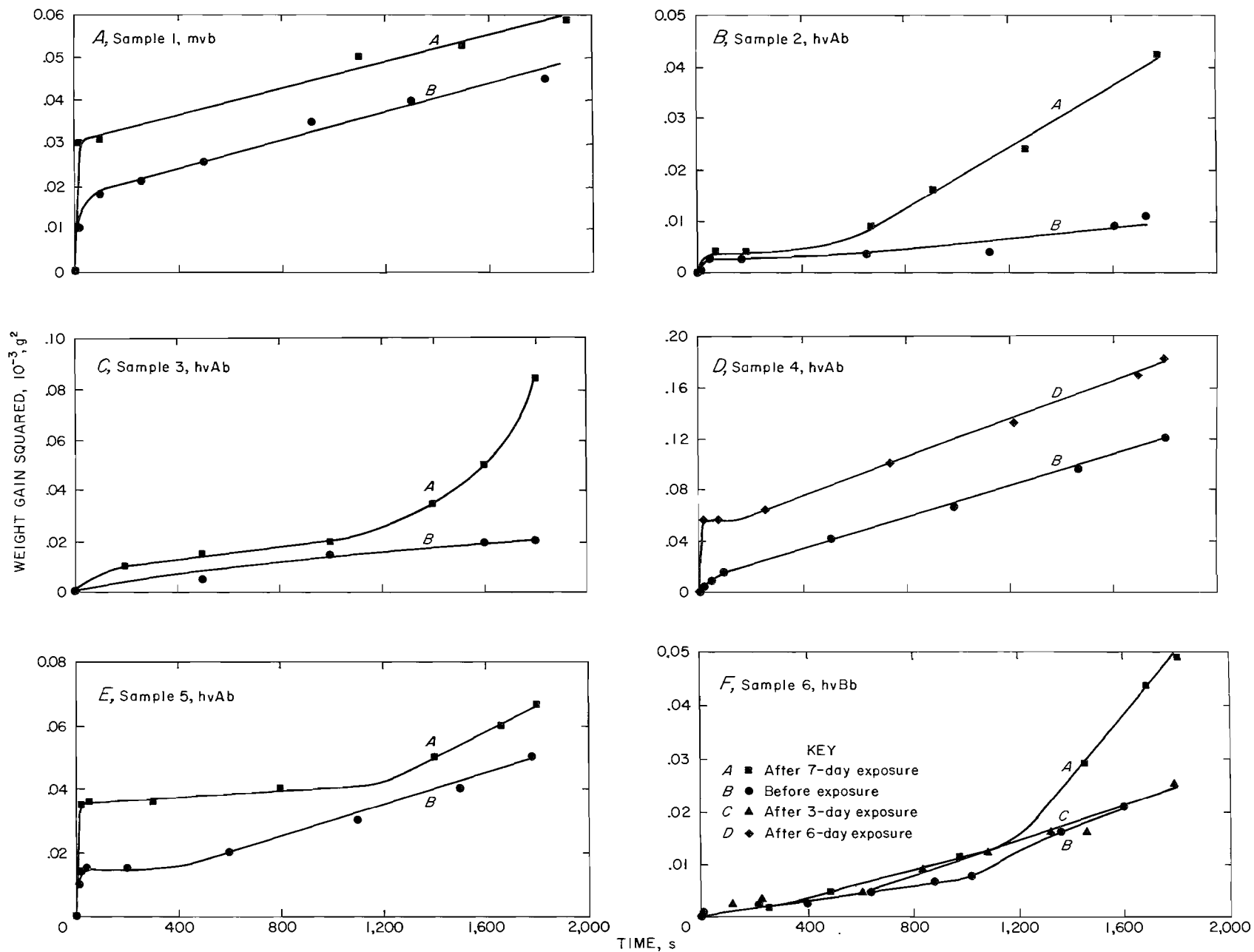
Figure 4.—Washburn plots of capillary penetration wetting results for minus 200-mesh bituminous coals in distilled-deionized water before and after exposure to ambient air atmosphere.
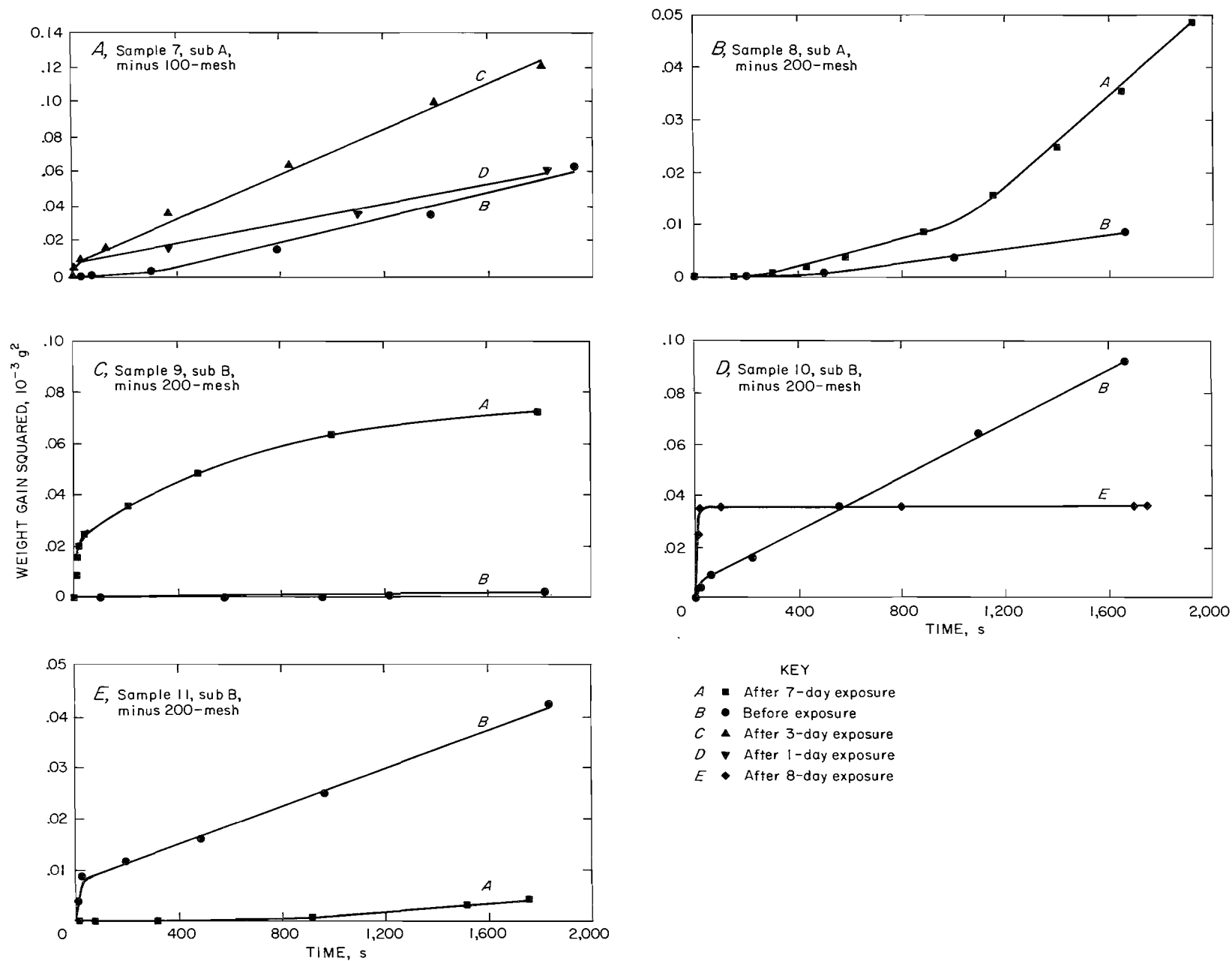
Figure 5.—Washburn plots of capillary penetration wetting results for subbituminous coals in distilled-deionized water before and after exposure to ambient air atmosphere.
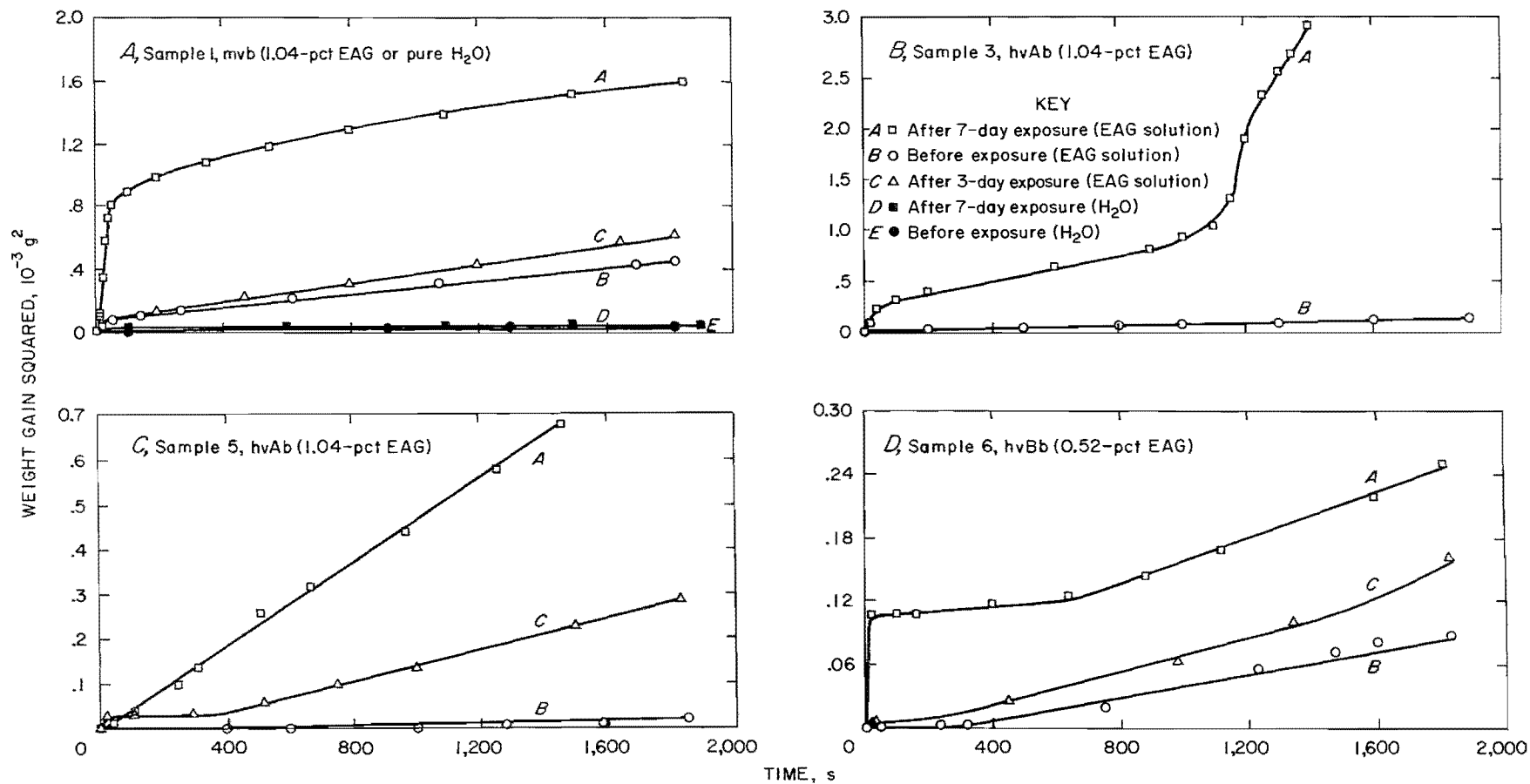
Figure 6.—Washburn plots of capillary penetration wetting results for minus 200-mesh bituminous coals in EAG nonionic surfactant solutions before and after exposure to ambient air atmosphere.

Figure 7.—Washburn plots of capillary penetration wetting results for subbituminous coals in EAG nonionic surfactant solutions before and after exposure to ambient air atmosphere.

Figure 8.—Washburn plots of capillary penetration wetting results for minus 200-mesh coals in 0.68-pct SDHS anionic surfactant solutions before and after exposure to ambient air atmosphere.

A, Sample 2, hvAb, 0.61-pct SD2ES

B

A

1.20
.96
.72
.48
.24
0

B, Sample 4, hvAb, 0.82-pct SD2ES

B

E

0.50
.40
.30
.20
.10
0

C, Sample 5, hvAb, 0.61-pct SD2ES

B

A

0.10
.08
.06
.04
.02
0

WEIGHT GAIN SQUARED, 10^{-3} g^2

D, Sample 8, sub A, 0.82-pct SD2ES

B

C

A

4.00
3.20
2.40
1.60
.80
0

E, Sample 10, sub B, 0.82-pct SD2ES

A

D

B

2.50
2.00
1.50
1.00
.50

400   800   1,200   1,600   2,000

F, Sample 11, sub B, 0.82-pct SD2ES

KEY

A □ After 7-day exposure
B ○ Before exposure
C △ After 3-day exposure
D ▽ After 2-day exposure
E ◇ After 6-day exposure

A

B

8.00
6.00
4.00
2.00

400   800   1,200   1,600   2,000

TIME, s

Figure 9.—Washburn plots of capillary penetration wetting results for minus 200-mesh coals in SD2ES anionic surfactant solutions before and after exposure to ambient air atmosphere.
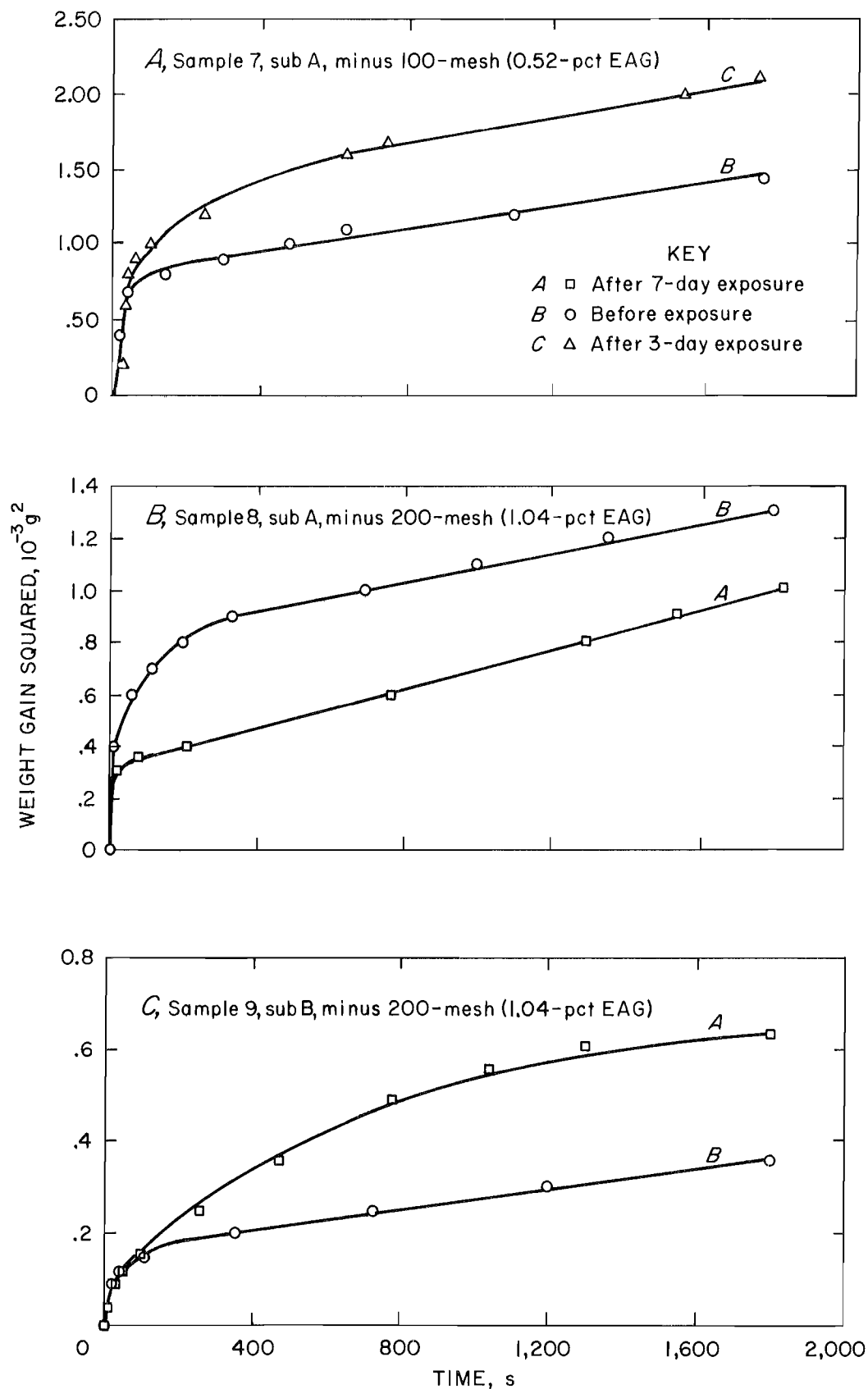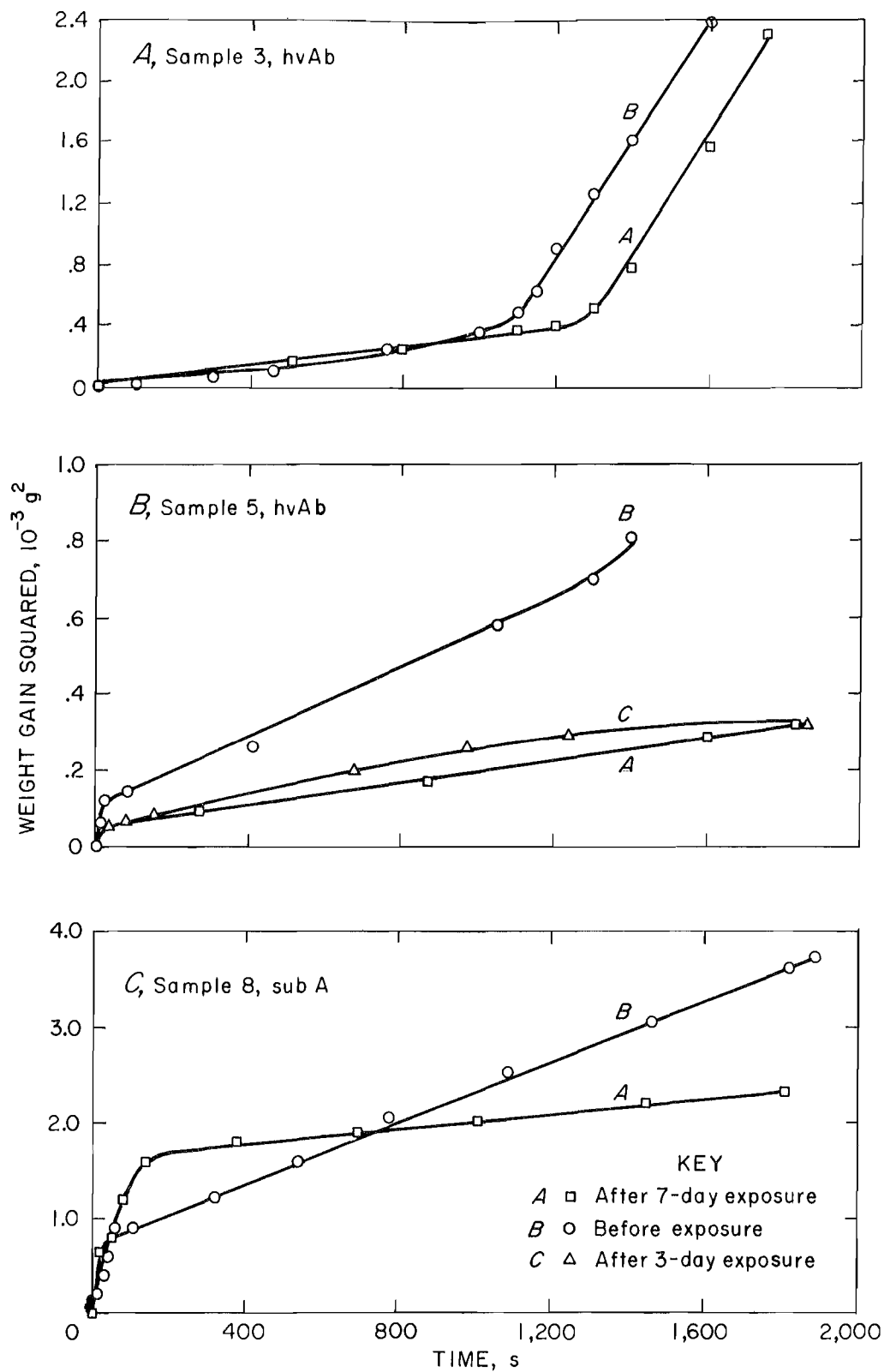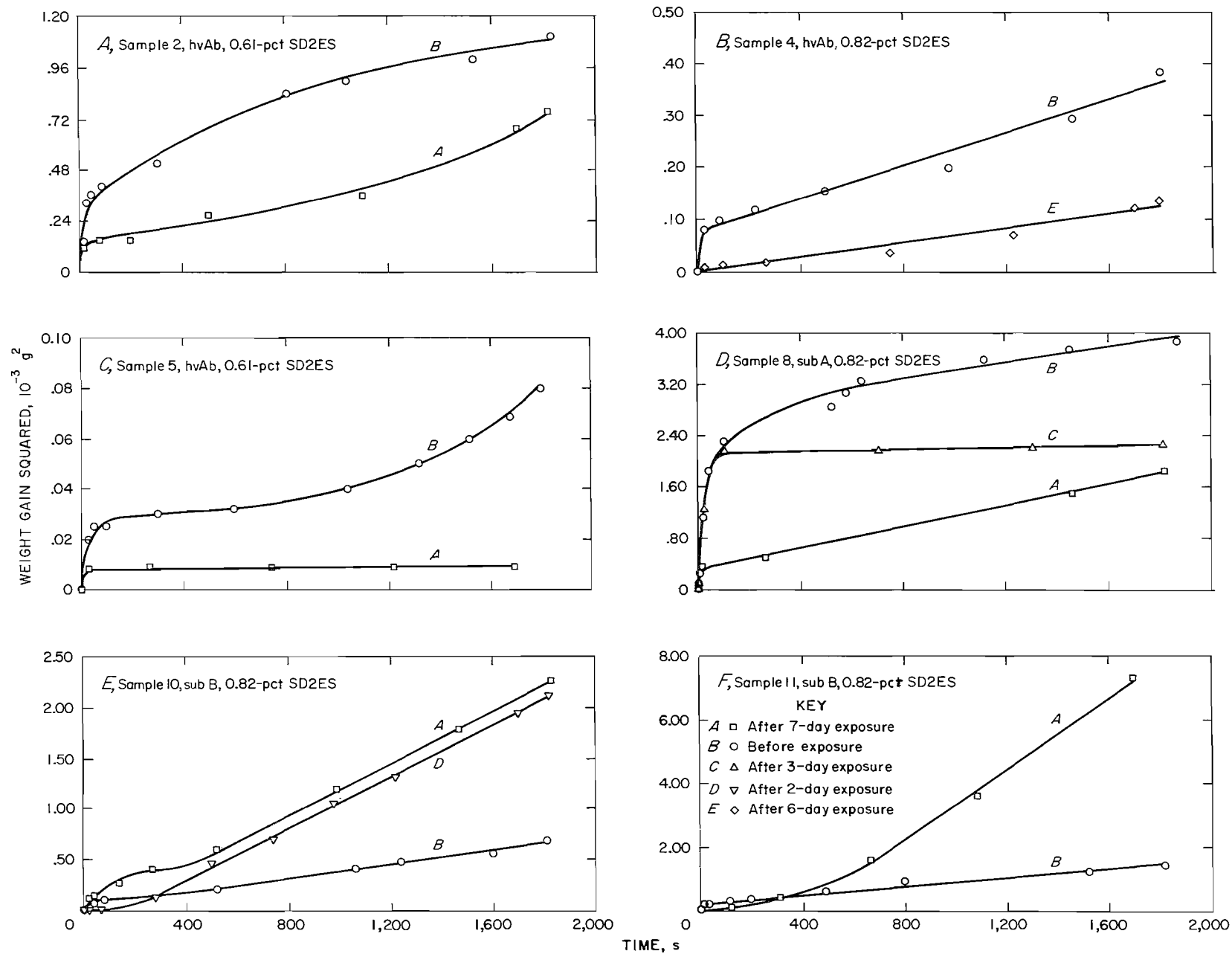
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B; figure 5C, curve A; figure 5D, curve B; figure 5E, curve B). The two-stage process could also have a reversed pattern with a very slow initial rate of imbibition followed by a rapid second stage occurring much later in the test (usually after 600 s and particularly noticeable in figure 4B, curve A; figure 4F, curves A and B; figure 5B, curve A). Frequently, the final stage of imbibition was postponed by an intermediate stage in which imbibition was temporarily suspended, only to resume abruptly after a period of time, to give a three-stage process (particularly noticeable in figure 4D, curve D; figure 4E, curves A and B). It is not known what causes these capillary wetting patterns for coal, but it can be seen that linear behavior, as predicted by the Washburn theory, rarely occurs over the total 30-min period of the experiment. However, linearity does occur in portions of the curves, particularly in the later stages of wetting after 600 s.

It is to be noted that to obtain a significant change in wetting response for high-purity water, an exposure of more than 3 days was required in the case of sample 6 coal (fig. 4F), but 3 days was sufficient in the case of sample 7 coal (fig. 5A). Generally, the weight of high-purity water imbibed into the coal column increased after a prior period of exposure to the air atmosphere (figs. 4-5). The exceptions were the two low-ranked (subbituminous B) coals, samples 10 and 11. These coals showed a decreased ability to absorb high-purity water after 8 and 7 days of exposure, respectively (figs. 5D-5E).

Capillary penetration tests, before and after exposure to air atmosphere, were performed on seven of the coal samples using EAG nonionic surfactant as the wetting solution. The wetting results are again presented as Washburn plots in figures 6 and 7. Generally, the curves exhibited two-stage wetting behavior. All of the coals except one (sample 8, fig. 7B) showed increased imbibition of EAG surfactant solution after exposure to ambient air atmosphere. This result is similar to that for high-purity water. However, the magnitudes of the effects were usually much greater for the surfactant solutions compared with high-purity water, as demonstrated in figure 6A, where wetting results for high-purity water (curves D-E) are included in the plot along with the curves for EAG surfactant solution (curves A-C) for comparison.

Anionic surfactant wetting solutions demonstrated capillary wetting behavior after exposure opposite to that of high-purity water and nonionic surfactant solutions. For SDHS, capillary wettability was decreased after exposure to the ambient air atmosphere for the three coals tested (fig. 8). For SD2ES surfactant solution, capillary wettability was decreased after exposure for four of the six coals tested (figs. 9A-9B). The two exceptions, which showed increased wettability after exposure, were the low-ranked coals, samples 10 and 11 (figs. 9E-9F). These same two low-ranked coals were the only coals to give decreased wettability in high-purity water after exposure to the air atmosphere (figs. 5D-5E).

DISCUSSION

FALLIBILITY OF CAPILLARY WETTABILITY TESTS PERFORMED ON EXPOSED COALS

It is evident from the experimental results that evaluating the capillary wetting performance of surfactant solution applied to different coals is a difficult task to perform accurately and in a manner that will realistically reflect the practical application of the wetting agent at the minesite or elsewhere. This is apparent from figures 4 through 9, in which the capillary wetting response is seen to be heavily dependent on how a given coal responds to atmospheric exposure. As mentioned earlier, for the most part, coals wetted with high-purity water or EAG nonionic surfactant solutions responded to atmospheric exposures by displaying apparent increased capillary wettability. This result is confounded by results with the anionic surfactants SD2ES and SDHS, which demonstrated an opposite wetting response on exposed coal, i.e., generally becoming less effective as coal-wetting agents, except for the lowest ranked coals tested.

This latter wetting behavior, in which the coal surface after exposure to air is apparently made less wettable, may be described as autophobic (7). Autophobicity is the tendency for a liquid to make a surface nonwettable despite possessing a surface tension below that of the critical value

for a given surface.[6] Such unexpected behavior can occur from adsorption of amphipathic[7] molecules from solution. It is to be noted that the surface tensions of the surfactant solutions used in this work measured in the range of 25 to 30 dyn/cm, which is considerably below the critical surface tension of 45 dyn/cm for all coals, as determined by Parekh and Aplan (8). Therefore, coal exposure to air apparently influences the adsorption of the wetting solutions in some manner, since the liquid surface tension of the surfactant solutions would have remained constant between wettability tests of coal before and after exposure.

In earlier work, a different type of autophobic behavior for anionic surfactants was discovered when anionic surfactant was applied to certain easy-to-wet coals (9). In this type of autophobicity, a depression in coal wettability was observed when SD2ES surfactant was used, compared with pure water alone, despite the greatly reduced surface

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[6]Critical surface tension is defined as the liquid surface tension required for spontaneous spreading of the liquid over a solid surface.

[7]Surfactants have a characteristic molecular structure consisting of a structural group that has very little attraction for water solvent (the hydrophobic group), together with a group that has strong attraction for water (the hydrophilic group). This is known as an amphipathic structure (5).

tension of the surfactant solution. Such behavior was not observed with the coals tested in this work, except for sample 5, a high-volatile A bituminous coal of high-ash and sulfur but low-oxygen content. The autophobicity appeared for the exposed coal wetted with high-purity water and with 0.61-pct SD2ES anionic surfactant solution, but not with SDHS anionic surfactant. Thus, after 1,400 s of capillary wetting time, 6.3 mg of water was imbibed (fig. 4E, curve A) compared with just 3.2 mg of SD2ES surfactant solution (fig. 9C, curve A).

The combination of autophobic anionic surfactant behavior and improved nonionic surfactant wetting after coal exposure can lead to confusing results when testing the capillary wetting response of various coals. For example, if anionic SDHS and nonionic EAG surfactants are tested on sample 3, high-volatile A bituminous coal before exposure to air, SDHS appears to be the superior wetting agent for this coal (fig. 10). On the other hand, if the same coal sample is exposed to the air for several days, EAG surfactant clearly becomes the wetting agent of choice. Another dramatic reversal in wetting performance between the same two surfactant solutions, applied to sample 5, high-volatile A bituminous coal, before and after exposure, is seen in figure 11. Again, capillary wetting results for unexposed coal favor SDHS anionic surfactant over EAG nonionic surfactant, but after exposure of the coal to air for 7 days, the EAG surfactant easily surpasses the anionic surfactant in wetting response. The wetting order of EAG surfactant with respect to 0.61-pct SD2ES was also inverted after coal exposure but less dramatically. It may be significant that sample 5 coal also exhibited autophobic response toward SD2ES anionic surfactant with respect to comparison with pure water at identical exposure times.

The reversal in wetting response occurring between anionic and nonionic surfactants after coal exposure was not necessarily the case with all coals. For the subbituminous A coal, sample 8, SDHS and SD2ES anionic surfactant wetting performances were depressed by exposure of the coal, but so was the performance of EAG nonionic surfactant (fig. 12). Therefore, the order of wetting with respect to anionic and nonionic surfactants remained unchanged in this case. However, the wetting abilities of the two anionic surfactants were changed with respect to one another, with the SD2ES capillary wetting response being depressed more severely by coal exposure.

These results point out the fallibility of exposed coal wettability testing and even call into question the validity of past investigations in coal wetting where care has not been taken to strictly control coal exposure before testing (usually the case). The present work has carefully controlled oxygen and nitrogen access to the coal samples, but moisture contents of the samples may have changed. Controlled humidity experiments are currently being performed to correct the latter deficiency.

INFLUENCE OF COAL RANK ON WETTABILITY AFTER EXPOSURE

Researchers investigating the spontaneous combustion of coals have observed the phenomenon to be related to coal rank, with the lower ranked coals tending to be more susceptible (10-11). Others have found that aqueous oxidation of coal decreases the hydrophobicity and flotation of coal, with the effect becoming greater as coal rank decreases (12). The possibility that wettability changes occurring after exposure are related to these combustion and flotation phenomena prompted a search for a relationship between coal rank and the wettability data acquired in this research. Accordingly, the weight changes (ΔW) for each type of coal in a particular wetting solution occurring as a result of exposure to air were computed at 1,400 s of elapsed wetting time in the capillary penetration tests. This wetting time was selected to avoid computing ΔW in weight-gain arrest regions (which usually occurred earlier in the test) and in regions where equilibrium had been reached (an exception was curve E of figure 5D, which apparently reached equilibrium almost immediately).

Thus,

$$\Delta W = W_x - W_o \qquad (5)$$

where ΔW = difference in weight gain, mg, measured at 1,400 s capillary wetting time, before and after exposure of coal to air atmosphere,

W_x = weight gain, mg, after X days of exposure to air atmosphere (usually 7 days), measured at 1,400 s wetting time,

and W_o = weight gain, mg, before exposure to air atmosphere, measured at 1,400 s wetting time.

The ΔW's calculated are listed in table 2. In cases where more than one coal of a given rank was tested, an average ΔW was calculated. Average ΔW's for each coal rank are plotted as bar graphs in figure 13 (high-purity water) and figure 14 (surfactant solutions).

The graph for EAG surfactant solution (fig. 14) shows a trend toward smaller ΔW as coal rank decreases. The graphs for high-purity water and SD2ES surfactant (figs. 13-14) do not show a readily discernible progressive decrease or increase in ΔW with coal rank. However, it is significant that the point at which ΔW passes from positive to negative for pure water (subbituminous A coal to subbituminous B, figure 13) is identical to the point at which ΔW passes from negative to positive for SD2ES surfactant solution (fig. 14). It is also significant that the anionic surfactant solutions, SD2ES and SDHS, display

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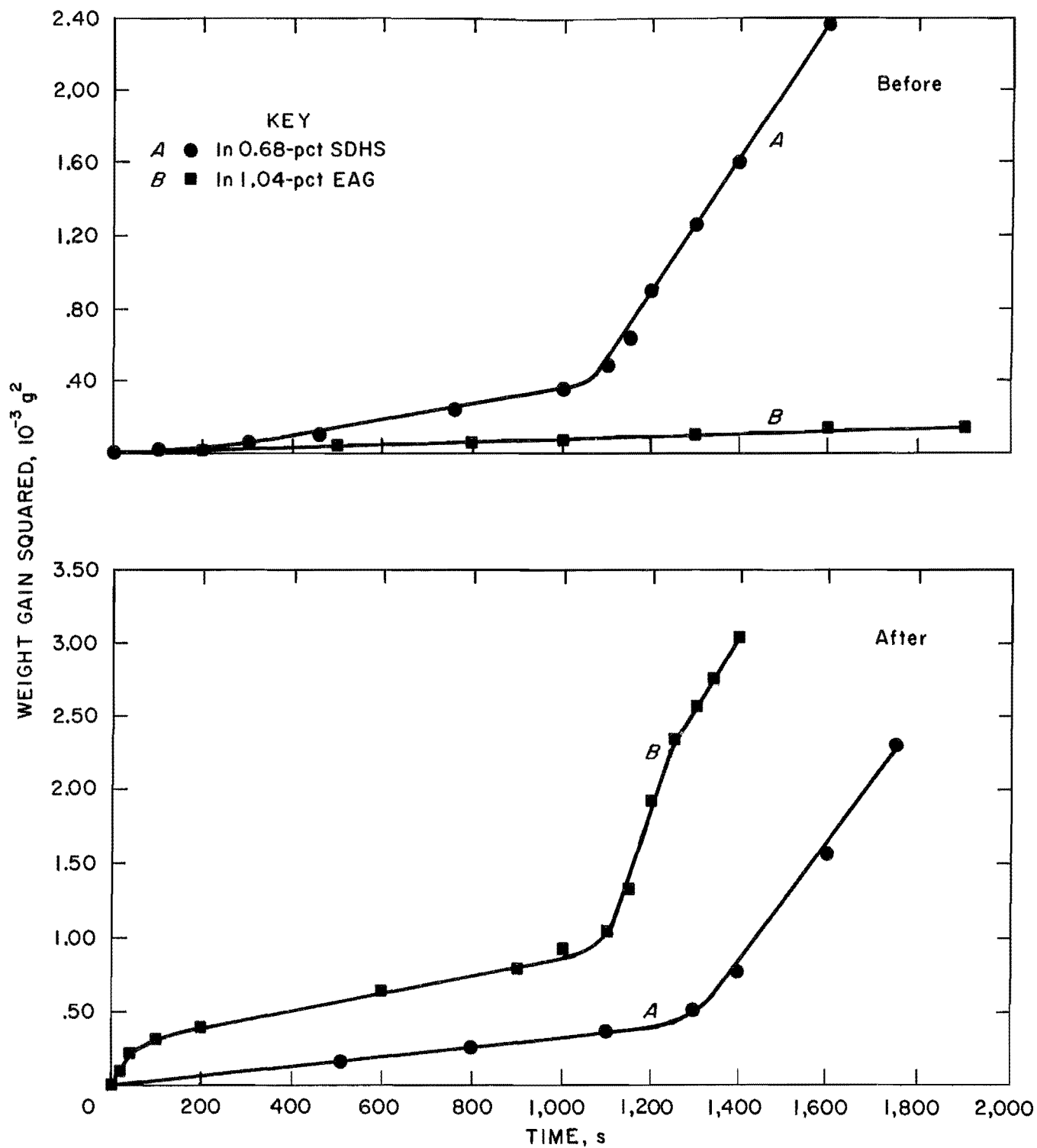
Figure 10.—Washburn plots of capillary wetting response for sample 3 (hvAb, minus 200-mesh) in surfactant solutions before and after 7-day exposure to ambient air atmosphere.
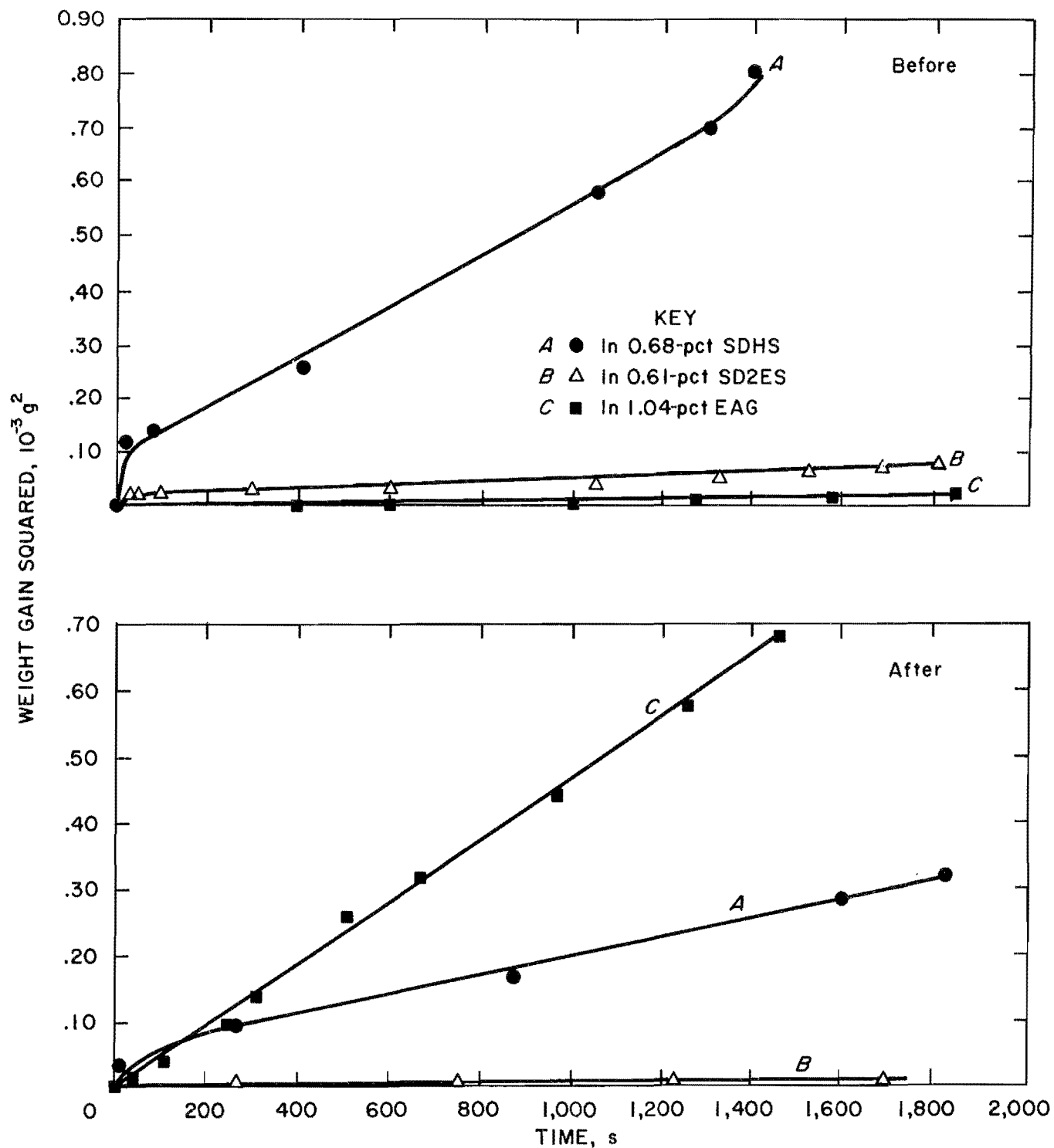
Figure 11.—Washburn plots of capillary wetting response for sample 5 (hvAb, minus 200-mesh) in surfactant solutions before and after 7-day exposure to ambient air atmosphere.
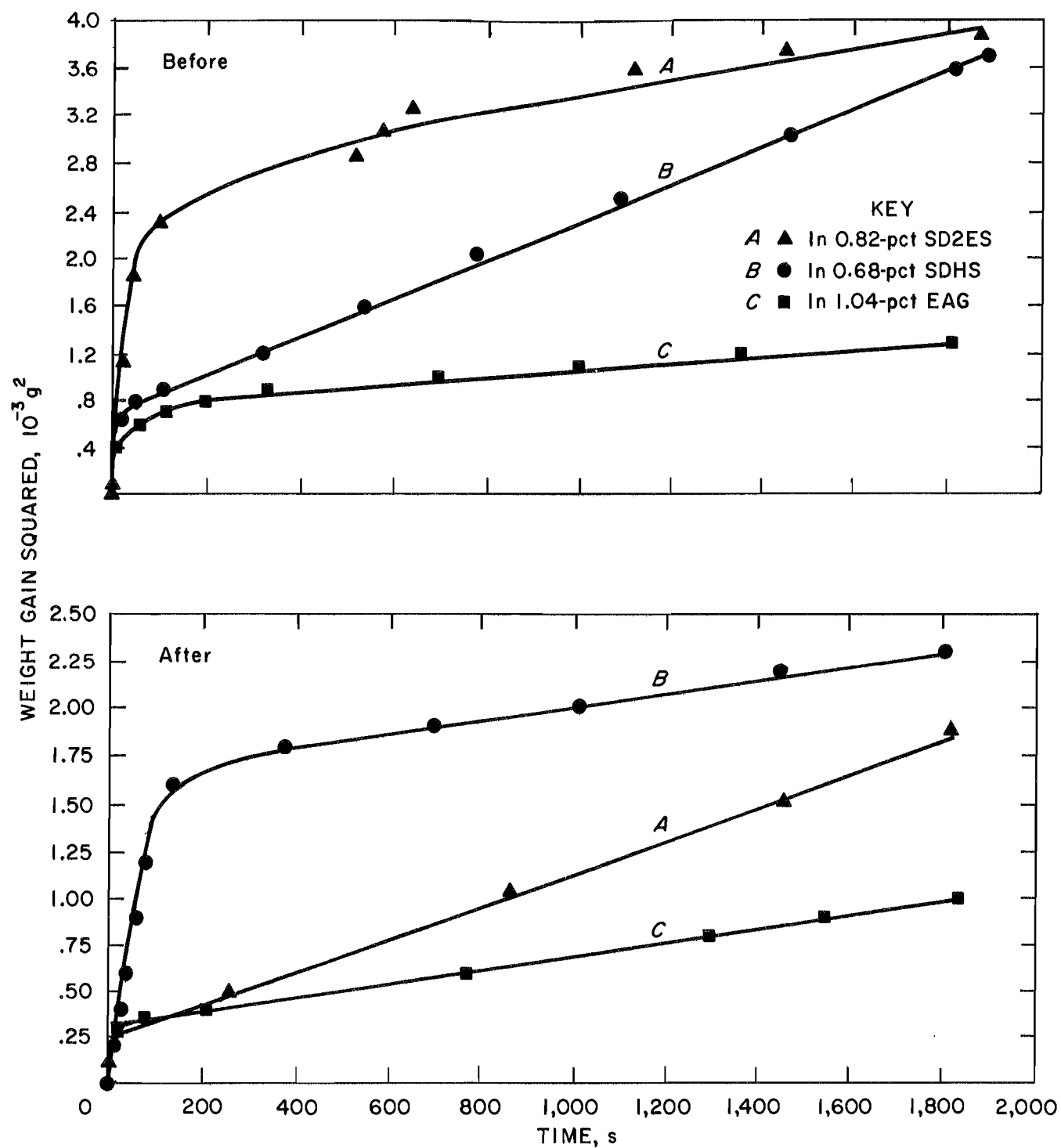
Figure 12.—Washburn plots of capillary wetting response for sample 8 (subA, minus 200-mesh) in surfactant solutions before and after 7-day exposure to ambient air atmosphere.
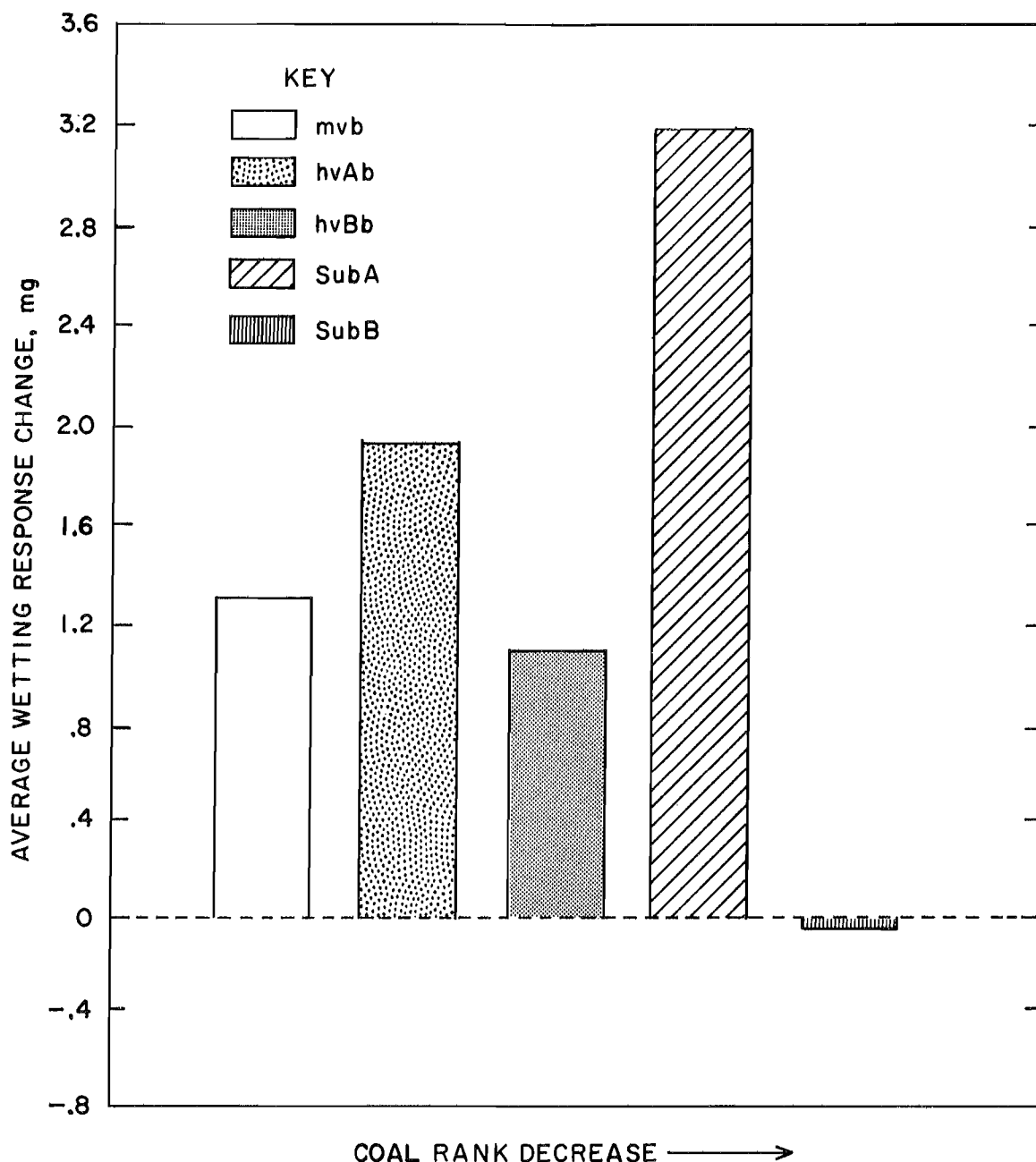
Figure 13.—Average wetting response change (ΔW) as a function of coal rank in high-purity water.

wetting behavior with respect to coal rank that is the converse of that with pure water and nonionic EAG surfactant. Thus, for the high-ranked coals, the anionic surfactants display autophobic behavior upon exposure, while pure water and nonionic surfactant improve wetting. On the other hand, for the lowest ranked coals, anionic surfactants promote wetting after exposure, while pure

water and nonionic surfactant depress wetting. Coal rank, then, appears to be a factor in the change of wetting response after exposure but not without irregularities. The irregularities are to be expected, in any case, since coal-rank classifications are made on the basis of a variety of characteristics, some of which are not necessarily related to surface chemistry, such as Btu's of energy content (13).

Table 2.—Capillary wetting response changes (ΔW) of
various wetting solutions on minus 200-mesh coals
before and after exposure to ambient air
atmosphere for 7 days, milligrams

[ΔW computed at 1,400 s elapsed capillary wetting
time for each pair of tests (weight gain after
exposure minus weight gain before exposure)]

Sample	Rank[1]	H_2O	1.04 wt pct EAG	0.82 wt pct SD2ES	0.68 wt pct SDHS
1	mvb	1.3	19.0	ND	ND
2	hvAb	2.3	ND	[2]-8.5	ND
3	hvAb	2.5	45.0	ND	-13.0
4	hvAb	[3]2.3	ND	[3]-7.5	ND
5	hvAb	.7	22.0	[2]-4.5	-12.5
6	hvBb	1.1	[4]5.3	ND	ND
7[5] ...	subA	[6]3.9	[4,6]8.0	ND	ND
8	subA	2.5	-6.0	-21.5	-7.5
9	subB	7.1	2.0	ND	ND
10 ...	subB	[7]-3.0	ND	18.5	ND
11 ...	subB	-4.2	ND	39.0	ND
Average	hvAb	2.0	34.0	-6.8	-12.8
	subA	3.2	1.0	-21.5	-7.5
	subB	-.1	2.0	28.8	ND

ND   Not determined.
[1]mvb   Medium-volatile bituminous.
hvAb   High-volatile A bituminous.
hvBb   High-volatile B bituminous.
subA   Subbituminous A.
subB   Subbituminous B.

[2]0.61-wt-pct SD2ES.
[3]6-day exposure.
[4]0.52-wt-pct EAG.
[5]Minus 100 mesh.
[6]3-day exposure.
[7]8-day exposure.

INFLUENCE OF ADSORBED OXYGEN ON WETTABILITY OF COAL

It is known that finely powdered coals are oxidized in air at room temperature (14-15). The initial attack by oxygen in the air is thought to involve the formation of peroxidic complexes. Gutierrez-Rodriguez and Aplan sparged coal surfaces with oxygen gas underwater and found that the hydrophobicity of coal was decreased, presumably a consequence of surface oxidation (12). Therefore, it would seem plausible that oxidation complexes formed on the coal surface during exposure in the laboratory atmosphere might be responsible for the wettability effects observed in the present work.

Accordingly, the inherent oxygen content of the coal (i.e., that derived in situ during the genesis of the coal and taken as the oxygen analyses determined by difference in table 1) was plotted against the ΔW data of table 2. The rationale for this procedure was as follows: If oxidation occurring on the coal surface during exposure significantly affects wettability, then it is reasoned that the inherent oxygen content of the coal should correlate with wettability effects. Thus, since coals of higher inherent oxygen contents are more susceptible to oxidation, then these coals should oxidize more readily upon exposure to air and demonstrate greater changes in ΔW.
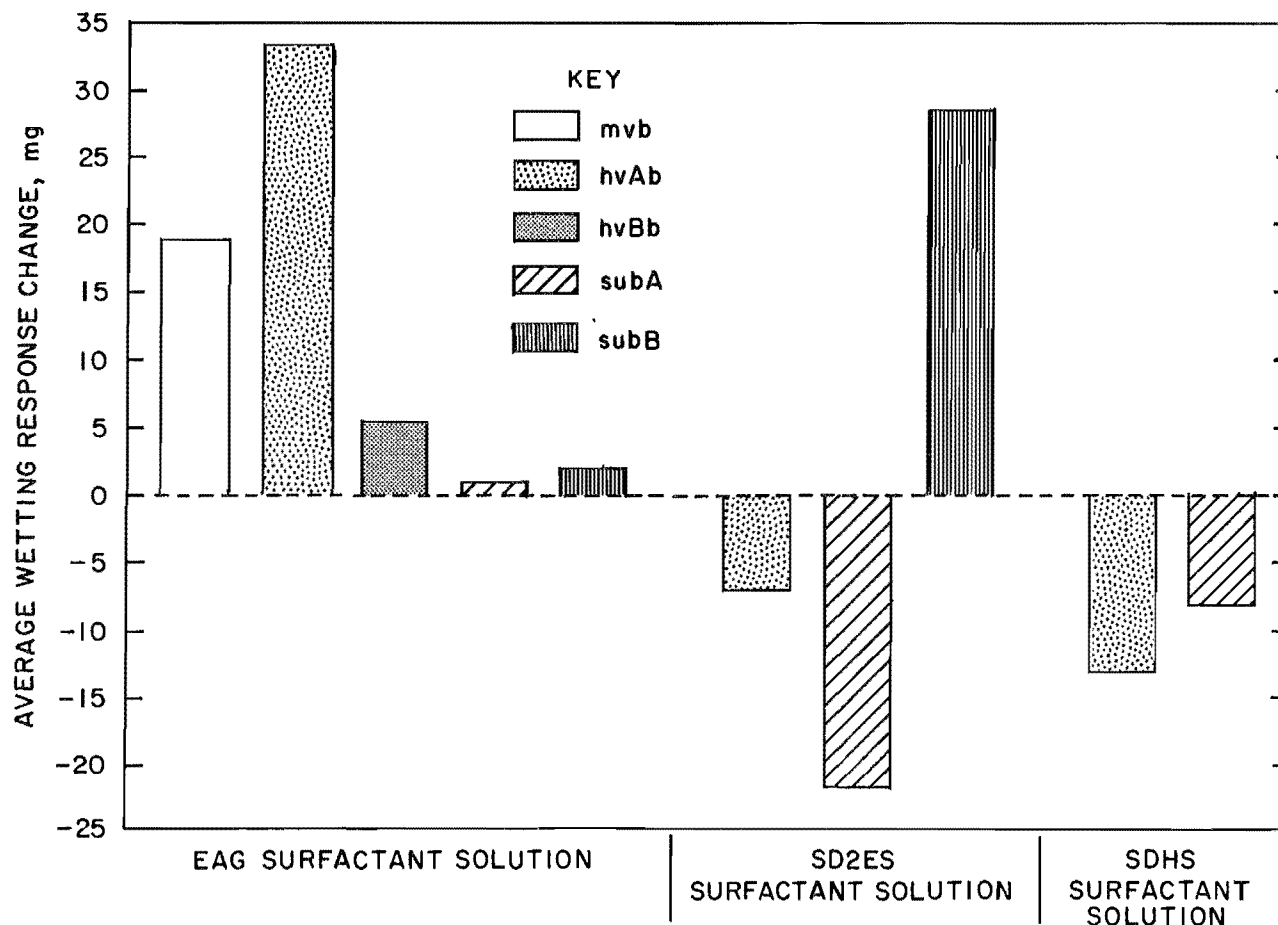

Figure 14.—Average wetting response change (ΔW) as a function of coal rank for nonionic and anionic surfactant solutions.

However, the resulting plot (not shown) of inherent oxygen versus ΔW showed a scatter of random data points and no evidence of order or correlation with ΔW wettability. This evidence contrasts with spontaneous combustion studies of coals in which increased reactivity was observed for coals of higher oxygen content (10). There was also no correspondence with aqueous oxidation studies on coals, where surface oxidation was determined to proceed much more rapidly on low-ranked coals, which usually have high inherent oxygen contents (12). The trend of much of the data from the present work indicates that the change in surface hydrophobicity occurring after exposure (ΔW) often tends to be smaller for lower ranked coals (EAG surfactant solution responses in figure 14, and the response of pure water toward subbituminous B coals in figure 13). This result is opposite to that expected on the basis of surface oxidation effects.

It is to be noted, however, that an orderly increase in the W_x and W_o wettabilities (but not ΔW) did occur with increasing inherent oxygen content of the coals. Therefore, it might be argued that inherent oxygen formation in coals and surface oxidation of coal upon exposure are different, and therefore, no relationship need exist between the two. There is evidence in the literature supporting this viewpoint. Gutierrez-Rodriguez and Aplan observed a difference in contact angles between in situ oxidized raw coals and coals oxidized by sparging with oxygen gas in water (12). They inferred that oxygen formed on the coal surface by aqueous oxidation in the laboratory may be different from that introduced during genesis of the raw coal.

However, the evidence that weighs most heavily against the surface oxidation origin for ΔW wettability changes is the negative changes in ΔW that were observed in the present work (table 2). One would predict from the surface oxidation conjecture that exposure should produce either oxidation of the surface and, hence, improved hydrophilicity and wettability or, at worst, no oxidation and therefore no change in wettability. But the data in table 2 and figures 13 and 14 indicate that exposure of coal can be significantly harmful to wettability in a number of cases so that negative wettability ($-\Delta W$) is produced. This autophobic behavior upon exposure, particularly in the pure water tests, would seem to require deoxidation of the coal surface, but the oxidizing conditions of the experiment exclude this possibility. Therefore, it is concluded that the ΔW wettability effects observed in this work are not directly related to coal surface oxidation occurring during the brief periods of air exposure (8 days or less). ·

INFLUENCE OF COAL COMPOSITION ON WETTABILITY

The influence of ash, carbon, and sulfur content on ΔW was determined using the same procedure applied previously to inherent oxygen content. The ΔW after exposure, calculated at 1,400 s wetting time, was plotted (not shown) against the ash, carbon, and sulfur contents (table 1).

There were no correlations or order visible in these plots. However, as with inherent oxygen, there was a correlation between the wettability W_o and W_x (but not ΔW) and ash content of the coal in anionic surfactant solutions. However, unlike with inherent oxygen, the wettabilities decreased with ash content, rather than increased. This result is roughly in agreement with the capillary rise data of Kost (16) for 32 different coals wetted with SDHS surfactant solution. The ash content influence, along with the inherent oxygen effect, may be a factor in anionic surfactant autophobicity in the exposure testing and will be discussed briefly later. The influence of ash content in general will be discussed at length in a subsequent Bureau report.

INFLUENCE OF SURFACE MOISTURE ON WETTING OF COAL BY PURE WATER

The coals, upon exposure, were subject to adsorption of moisture from the ambient air atmosphere or desorption of the inherent moisture in the coal. It is likely that adsorption or desorption of moisture is dependent on the inherent moisture of the coal, which, in turn, may influence the coal surface wettability. Accordingly, the weight gains before exposure (W_o) and after exposure (W_x), measured at 1,400 s of capillary wetting time in pure water, were plotted against the inherent moisture content of the coal from table 1. The plot is presented in figure 15 with "before exposure" represented by curve B and "after exposure" represented by curve A. Exposure of coal is seen to consistently improve the wettability of coal with pure water, until the inherent moisture is around 18 pct. The surface assumes a more hydrophobic character after exposure for coals of greater inherent moisture content. The fact that the before- and after-exposure curves below 18 pct moisture in figure 15 resemble each other in shape suggests that essentially minor changes have occurred on the coal surface as a result of exposure.

Bernett and Zisman (17-18) discovered that high-energy surfaces such as borosilicate glass, fused quartz, and alpha alumina have the same critical surface tension at a given relative humidity. As relative humidity is increased, the critical surface tension decreases. They concluded that the wettability and critical surface tension were principally determined by a film of water physically adsorbed on the surface of the solid and not by the nature of the solid substrate. Parekh and Aplan (8), using the method of Bernett and Zisman, determined the critical surface tension of all coals as 45 dyn/cm. They suggested that the constancy of the critical surface tension for all types of coals could be attributed to adsorption of a film of moisture. In the present work, the coal surface is conceived of as a composite of high- and low-surface-energy components. The high-energy components are derived from impurities, such as quartz and clays, and from oxidation of the coal matrix (during genesis in situ and/or by exposure to the atmosphere after mining). The low-surface-energy components derive from the organic coal matrix itself. If Parekh and
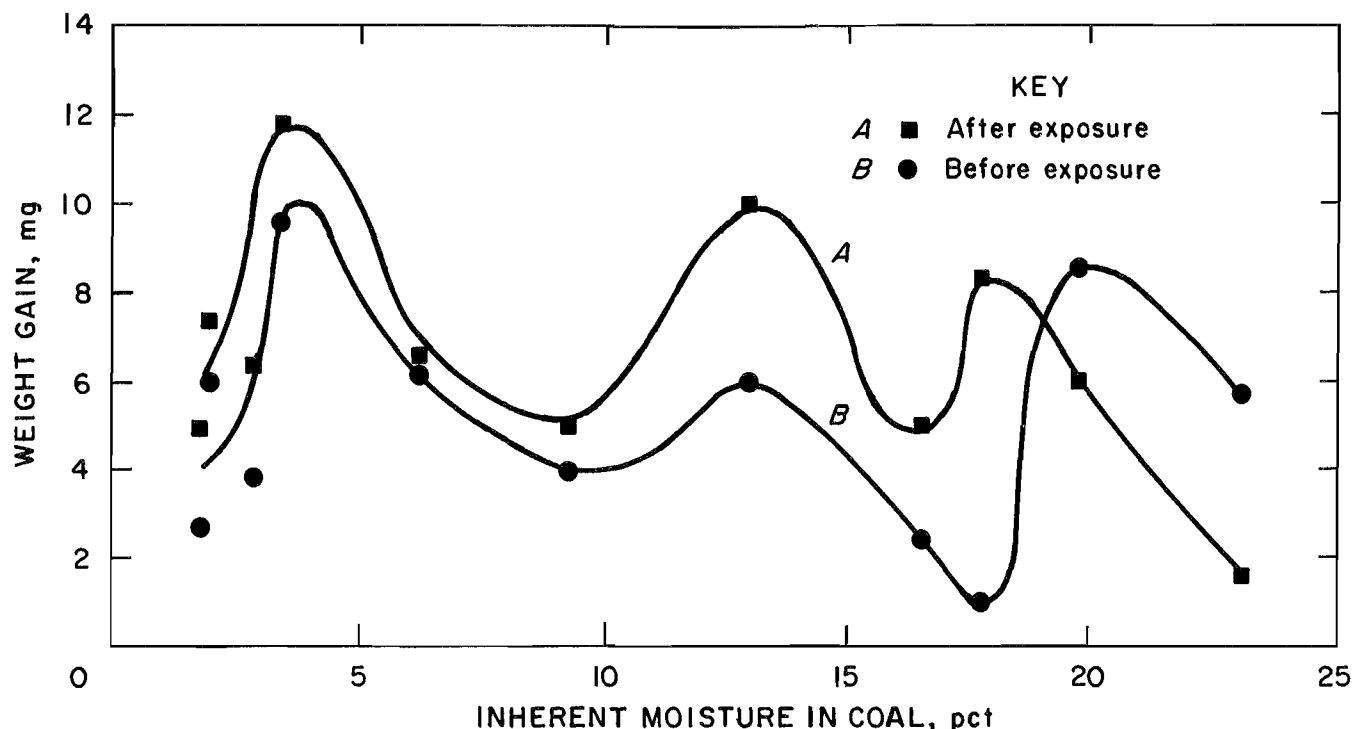
Figure 15.—Influence of inherent moisture content of coals on capillary wetting response in pure water before and after exposure (usually 7 days) to ambient air atmosphere. (Measured at 1,400 s wetting time.)

Aplan are correct, then it would seem that physical adsorption of water occurs on low-energy surfaces of the coal as well as high-energy surfaces. Practically speaking, the magnitudes of the wetting changes from moisture adsorption were small for pure water and of little practical consequence in the present work. However, the effect is important for understanding the wetting mechanisms involved with surfactant wetting solutions when the magnitude of the effect is substantial and serious difficulties in estimating surfactant wetting performance are encountered, as observed earlier.

In figure 15, the positive displacement of the exposed coal curve A from unexposed coal curve B in the region below 18 pct may be due to a film of adsorbed moisture that has been interposed between the coal surface and the wetting solution as a result of exposure. This film is seen not to particularly affect any interactions between the pure water wetting liquid and the coal surface but may aid the imbibition of wetting liquid into coal-column pore space by capillary action. This results in greater weight gain and, therefore, improved wettability of the coal.

The negative displacement occurring at inherent moistures greater than 18 pct could be caused by the attainment of an equilibrium between adsorbed surface moisture and moisture in the surrounding atmosphere. Therefore, above this critical point, moisture may begin to desorb from the coal surface into the surrounding atmosphere. Thus, there is a net loss of the surface film of water resulting in relatively less hydrophilic film available for

capillary action, which could give the apparent negative wetting displacement after exposure that is visible in figure 15 above about 18 pct moisture. This explanation of the wetting behavior must be considered tentative, however, until further testing under constant-humidity conditions is completed, since the coals were subjected to unknown humidity conditions in the present experiments.

The change in coal pore structure upon drying has been measured by observing the uptake of nickel cations for as-received and dried low-ranked coal (19). The dried coal was found to have a reduced capacity to adsorb nickel. This was judged to be due to a collapse of the coal gel structure resulting in the reduction of the number and size of pores and to water depletion from the pores followed by replacement with gas, which retards mass transfer of the nickel irons. Mraw (20) determined that only a portion of the total water in coal exhibits phase behavior similar to that of bulk water. The remainder of the water is confined to internal surfaces and very small pores and, perhaps, clusters around oxygen sites. The division between the two kinds of water in coal was found to be marked by a critical moisture content in the coal of 17 pct, which nearly coincides with the crossover point for ΔW in the present work. Mraw found that water in excess of 17 pct in coal behaves more like bulk water and that water less than 17 pct possesses different properties such as resistance to solidification by freezing. Evans' research (21) into the drying of brown coal of high moisture content (about 66 pct) revealed shrinkage in the number and size of pores as

drying proceeded. At about 14 pct moisture, shrinkage ceased and swelling of the pores was observed.

Therefore, it is suggested that the wetting phenomena observed in the region of 14- to 20-pct coal moisture in the present work may also originate from pore structure changes in the coal after exposure. The phenomenon of positive and negative displacement of wetting may be seen more clearly if the difference between the curves (ΔW) is plotted as a function of the percentage of inherent moisture in the coal (fig. 16). Again, the ΔW is measured at 1,400 s capillary wetting time. The maximum ΔW shown in figure 16 between 14 and 20 pct may be related to expansion of the coal pore structure due to loss of moisture into the atmosphere. In the region of >20 pct moisture, the hydrophobic behavior after exposure may be related to coal pore structure collapse as well as to possible decreased water film coverage due to moisture loss into the surrounding atmosphere.

INFLUENCE OF SURFACE MOISTURE
ON WETTING OF COAL BY
SURFACTANT SOLUTIONS

Anionic surfactant solutions tended to demonstrate capillary wetting behavior that was the reverse of wetting behavior with pure water with respect to coal exposure and inherent moisture content. Displacement of the before and after exposure curves was of large magnitude, and the wetting action of both SDHS and SD2ES surfactants was repressed by exposure at less than 18 pct inherent coal moisture (fig. 17). Again, the weight gains selected to be plotted against inherent moisture were those at 1,400 s capillary test wetting time. Because there were insufficient data to properly draw the curves for SDHS solution, those curves are drawn as dashed lines in figure 17 and conform to the shape of the SD2ES curves on the figure. This discretionary interpretation is based on consideration of the nearly similar chemical structures of the two sulfosuccinate compounds. It is a reasonable supposition to expect the capillary wetting by these two surfactants to be essentially the same, except for the magnitude of response on a given coal.

As shown in figure 17, at greater than 18 pct inherent coal moisture, exposure of the coals causes positive displacement of the before and after curves for SD2ES so that apparent improvement in capillary wetting after exposure is achieved. As observed previously for coals wetted with pure water (figs. 15-16), the surface characteristics of coals with inherent moisture in the range 14 to 20 pct are evidently changed greatly after exposure to the atmosphere. This feature is more clearly seen in figure 18, where the displacements (ΔW) between the curves of
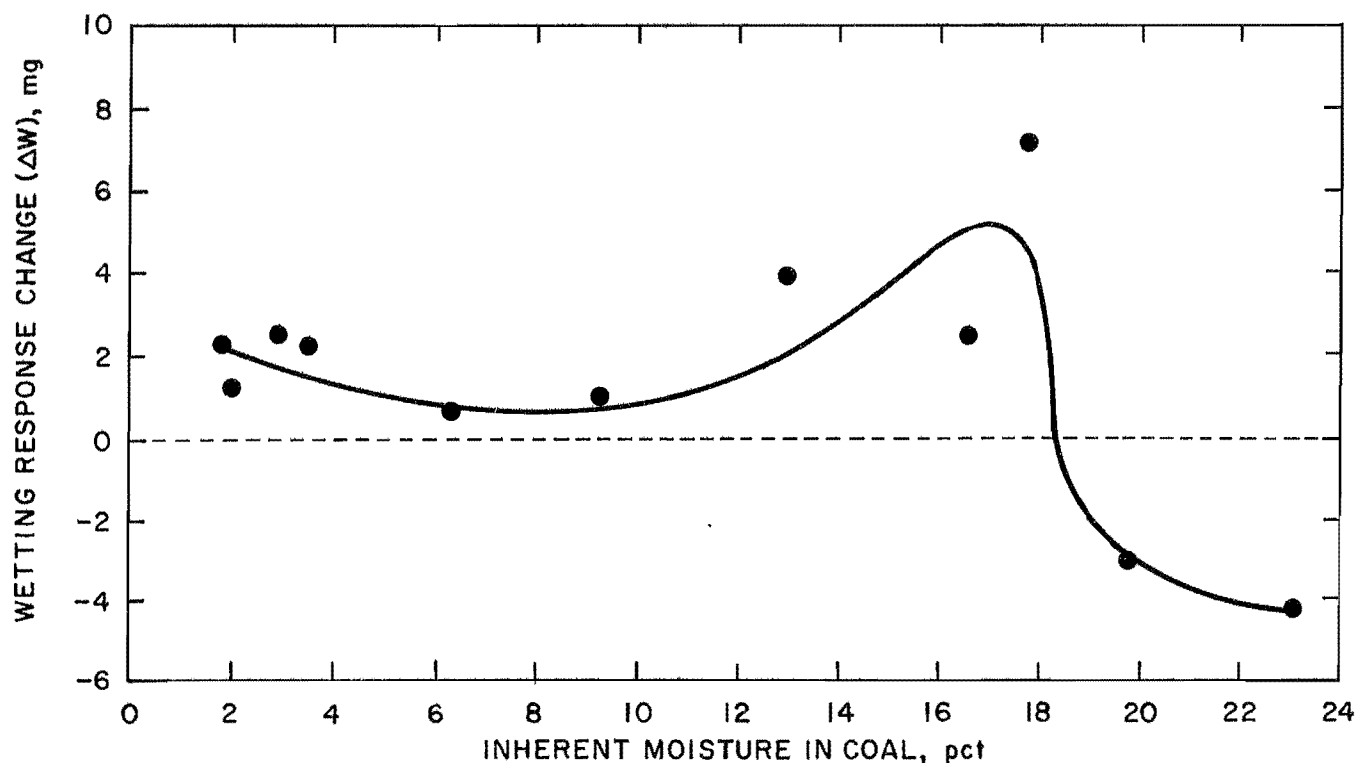

Figure 16.—Influence of inherent moisture content of coals on capillary wetting response change (ΔW) in pure water after exposure to ambient air atmosphere. (Measured at 1,400 s wetting time.)
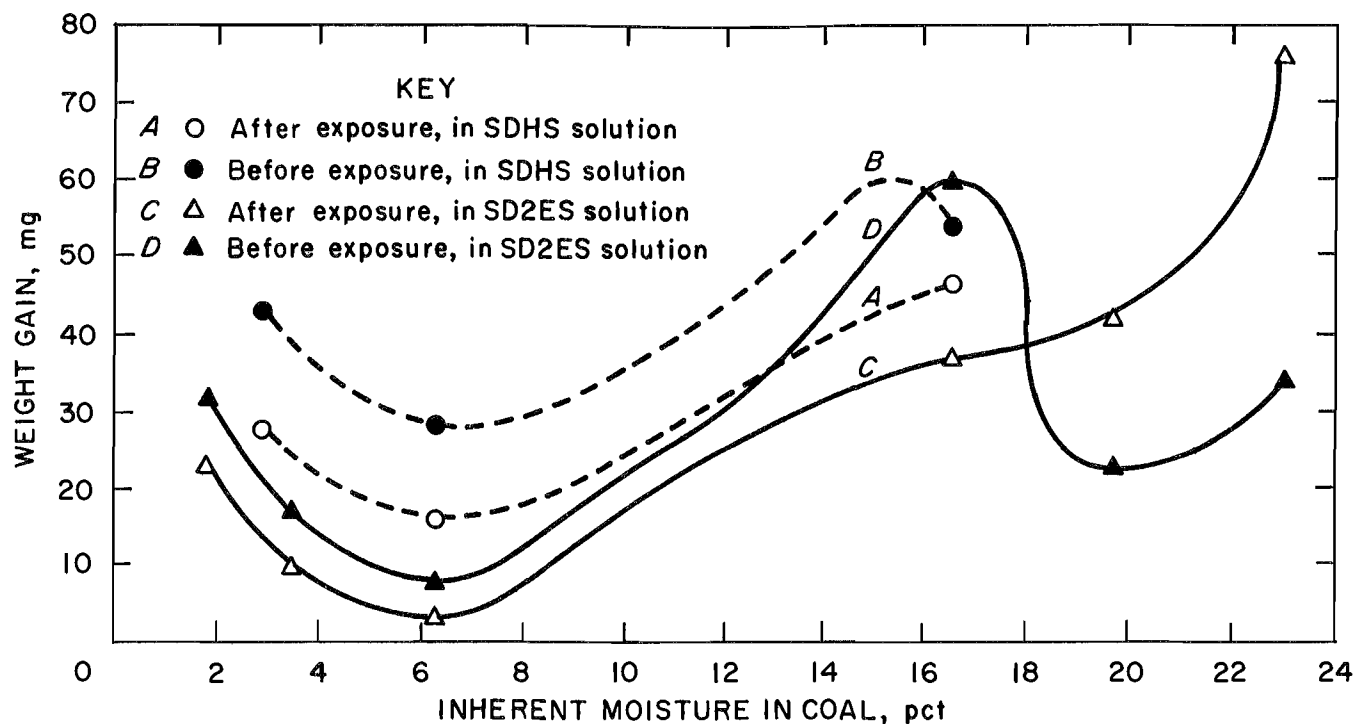
Figure 17.—Influence of inherent moisture content of coals on capillary wetting response in SD2ES and SDHS anionic surfactant solutions before and after exposure to ambient air atmosphere (usually 7 days). (Measured at 1,400 s wetting time.) Surfactant concentrations were 0.68-pct SDHS and 0.82-pct SD2ES, except for coals of 1.8 and 6.3 pct inherent moisture where 0.61-pct SD2ES was used.
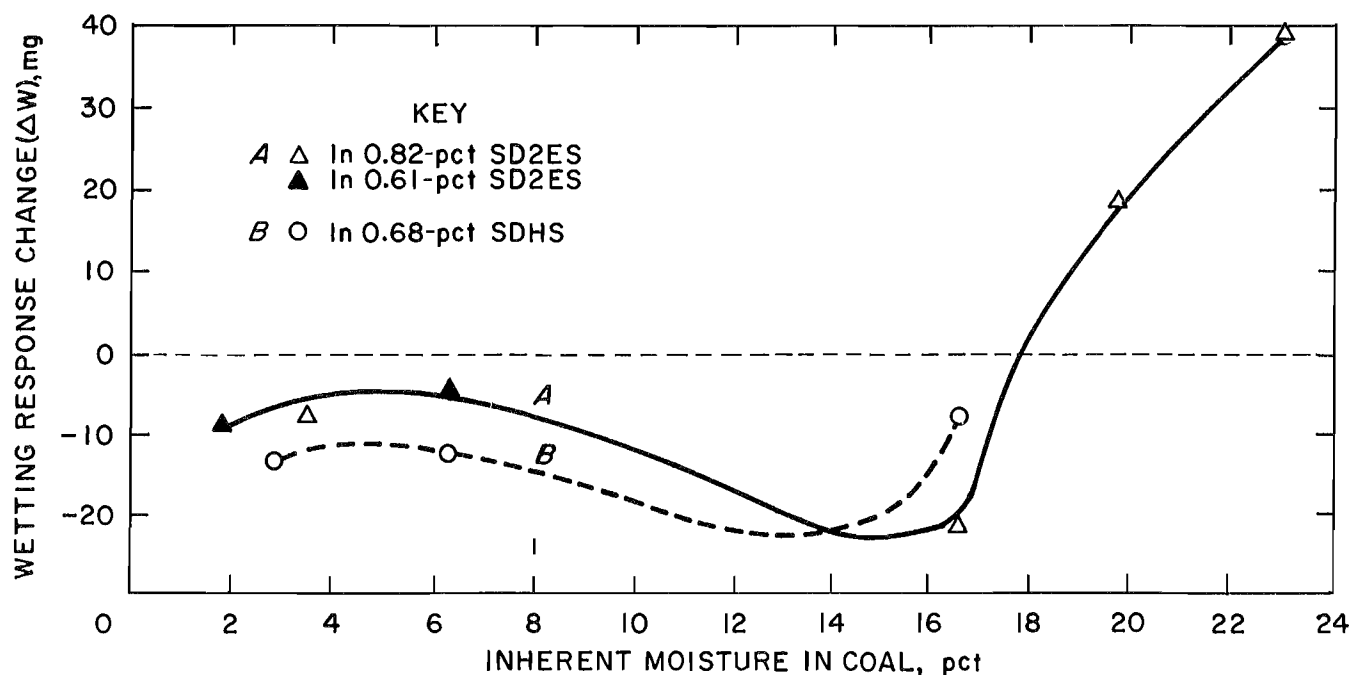

Figure 18.—Influence of inherent moisture content of coals on capillary wetting response change (ΔW) in anionic surfactant solutions occurring after exposure to ambient air atmosphere. (Measured at 1,400 s wetting time.)

figure 17 and listed in table 2 are plotted against the concentration of inherent moisture in each coal. Once again, the discretionary nature of the SDHS curve in figure 18 is indicated by a dashed line. If the difference in magnitudes is ignored, the form of the ΔW curve for SD2ES surfactant solution in figure 18 (curve A) is approximately a mirrorlike reflection of the ΔW curve for pure water in figure 16. This correlation indicates that wetting by pure water and wetting by anionic surfactant solutions are related. It is suggested that the relationship originates from attraction of both liquids to hydrophilic sites on the coal surface, but the attraction of the anionic surfactants results in a conversion of these wettable sites to a hydrophobic state.

For EAG nonionic surfactant solution, the form of the weight-gain curve before exposure (fig. 19, curve B) resembles that for anionic SD2ES solution before exposure (fig. 17, curve C). On the other hand, after exposure, the EAG surfactant wettability curve (fig. 19, curve A) tends to be positively displaced from the before-exposure curve, giving a net improvement in capillary wettability of coals that have below 16 pct inherent coal moisture. In contrast, SD2ES surfactant solution is displaced negatively in this region, resulting in a net negative wetting response (fig. 17, curve D). Whereas EAG surfactant responds to each coal

similarly after exposure except for the large positive displacement at low inherent coal moistures (fig. 19, curve A), the curve shapes for SD2ES solution and pure water deviate greatly from the before-exposure curves in the region of 16 to 20 pct inherent coal moisture (fig. 17, curve D; fig. 15, curve A).

If the ΔW displacements for EAG surfactant solutions from table 2 are plotted versus the inherent coal moisture concentration, a fairly gradual decreasing trend in wettability after exposure is obtained as inherent coal moisture is increased (fig. 20). The data show considerable variation, but a reversal in wettability appears to occur at about 15 pct inherent coal moisture. However, this crossover from positive to negative wettability appears to be an extension of the gradual decline of wettability as inherent moisture is decreased, with none of the maximums, minimums, or other aberrations in ΔW that were displayed by pure water and anionic surfactant solutions. This behavior suggests that a different wetting mechanism may be dominating when EAG nonionic surfactant is applied to exposed coal, compared with pure water and SD2ES surfactant. In this wetting mechanism, it is suggested that the change in ΔW may depend heavily on the quantity of adsorbed moisture on the coal surface and may be relatively independent of the coal substrate beneath the film of
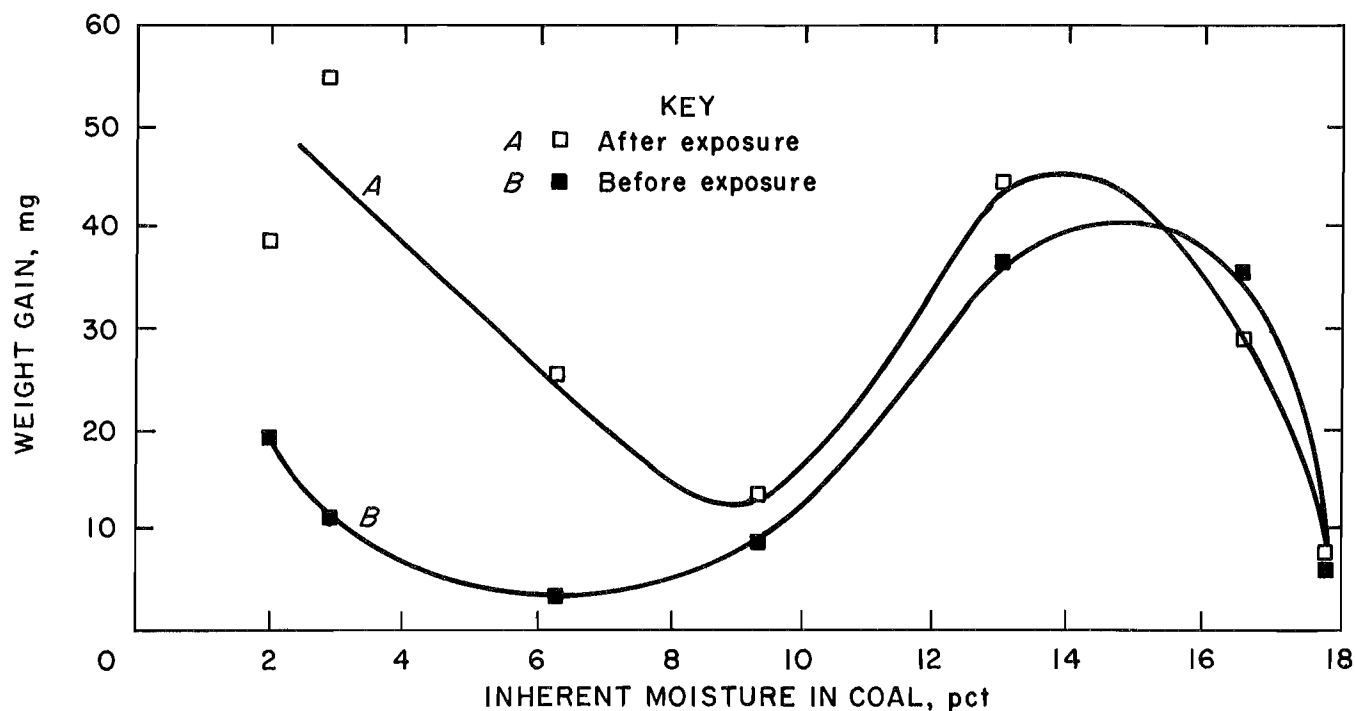

Figure 19.—Influence of inherent moisture content of coals on capillary wetting response in EAG nonionic surfactant solutions before and after exposure to ambient air atmosphere (usually 7 days). (Measured at 1,400 s wetting time.) Surfactant concentration was 1.04-pct EAG, except for coals of 9.3 and 13.0 pct inherent moisture where 0.52-pct EAG was used.
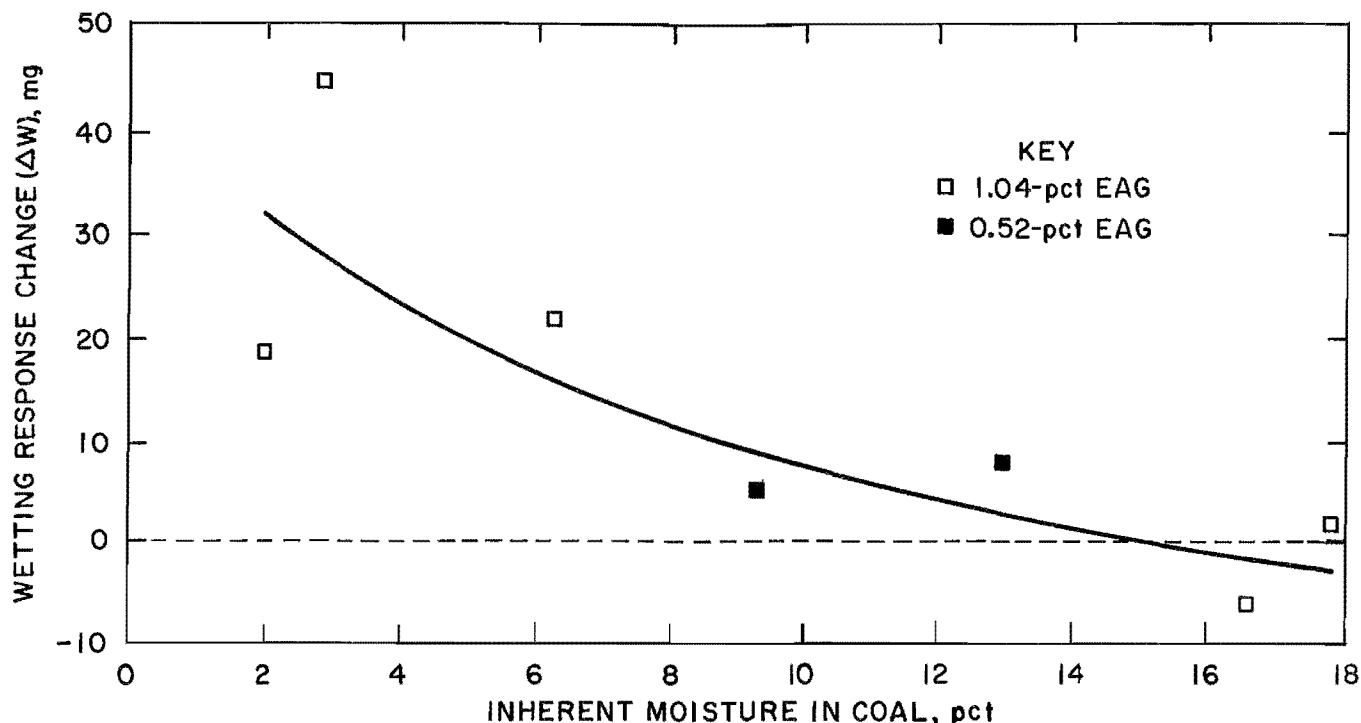
Figure 20.—Influence of inherent moisture content of coals on capillary wetting response change (ΔW) in nonionic surfactant solutions occurring after exposure to ambient air atmosphere. (Measured at 1,400 s wetting time.)

adsorbed water. Even possible changes in coal pore structure, which may occur in the region around 17 pct inherent coal moisture, appear to be inconsequential during wetting by this nonionic surfactant. From figure 20, one might predict that the lower the inherent moisture of the coal, the more likely it is that a larger amount of water will be adsorbed after exposure to the humidity of the surrounding atmosphere. If this is the correct interpretation, EAG surfactant appears to respond to this greater amount of adsorbed water after exposure by an increase in wettability response.

It is hypothesized that EAG surfactant responds to adsorbed moisture in the capillaries of the coal column by attaching to the moisture layer through hydrogen bonds formed with its numerous ethylene oxide groups. Ethylene oxide groups are known to form hydrogen bonds readily (5), and this action may dominate the change in wetting action on coal caused by exposure when EAG surfactant is used. In addition, hydrogen bonding through the acetylenic group of the EAG surfactant may also occur as a result of resonating triple bonds with the water molecules on the coal surface. Bernett and Zisman found higher critical surface tensions (equivalent to increased wettability) for aromatic hydrocarbon liquids on high-energy surfaces due to resonating double bonds of the benzene ring forming hydrogen bonds with adsorbed water molecules (17). Thus, adsorbed moisture on the coal after exposure

may help draw the wetting solution into the coal-column pores via hydrogen bonding and may also improve wetting by aiding the diffusion of EAG surfactant molecules to hydrophobic sites on the coal.

On the other hand, hydrophilic sulfonate groups, which are part of the SD2ES and SDHS anionic surfactant molecule, are known not to form hydrogen bonds (5). Therefore, the liquid front of the anionic surfactant solution might tend to be less affected by an adsorbed layer of water on the coal after exposure.

Plots of ΔW versus inherent coal moisture for all four wetting solutions employed are combined in figure 21 for comparison of the wetting effects described and to show the difference in magnitudes for the effects.

ADSORPTION ORIENTATION FACTOR FOR AUTOPHOBIC BEHAVIOR DISPLAYED BY ANIONIC SURFACTANTS

The wettability behavior of anionic surfactants after exposure of coals cannot be explained wholly on the basis of the appearance or disappearance of an adsorbed moisture film on the coal and its interaction with the hydrophobic film of anionic surfactant at the interface of adsorbed water and wetting solution. In earlier work (9), a great variability in wetting response was experienced when SD2ES anionic surfactant was used on a number of
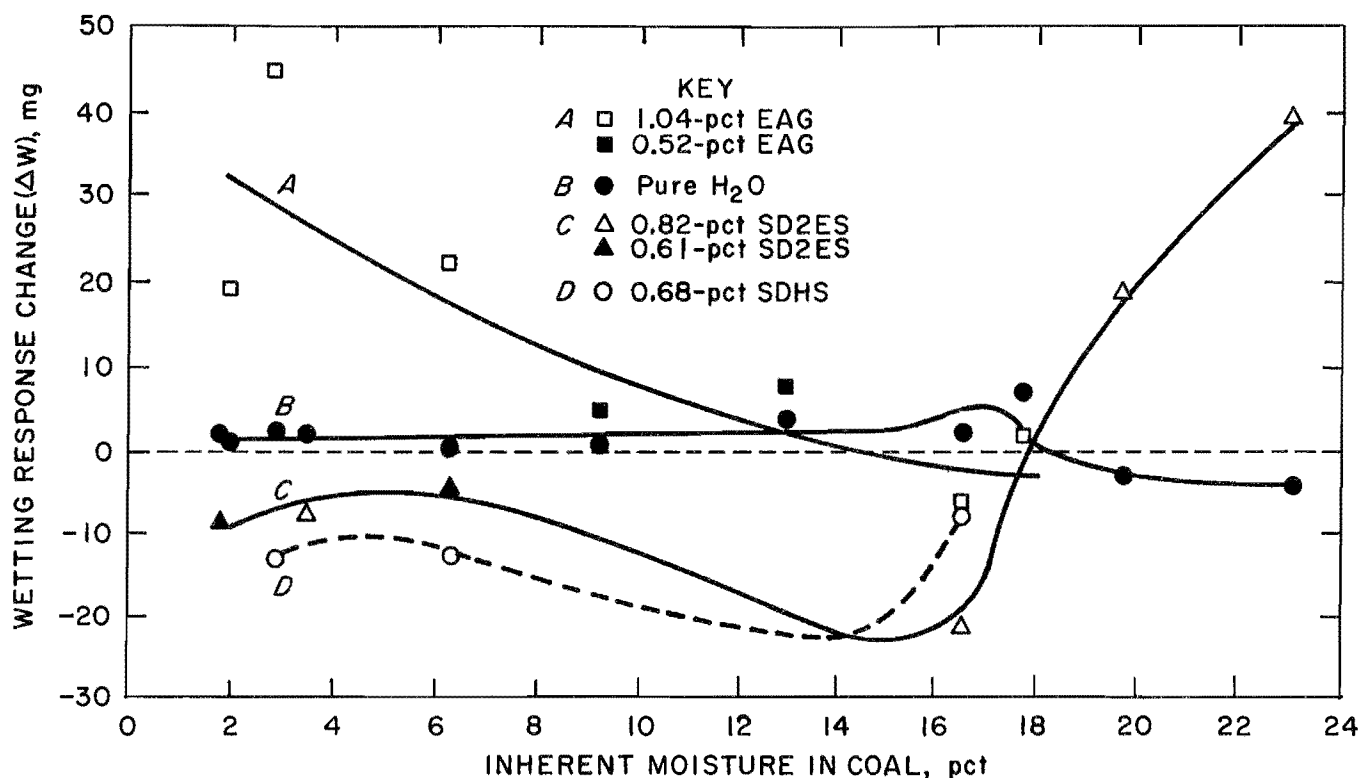
Figure 21.—Influence of Inherent moisture content of coals on capillary wetting response change (ΔW) In all surfactant solutions and pure water after exposure to ambient air atmosphere.

coals where exposure was not a factor. An ion-exchange model was derived to explain these variable experimental results with SD2ES.

Ion exchange is believed to occur directly between hydrophilic coal surface anion groups and surfactant anions or, alternatively, in an outer layer adjacent to an inner layer of secondary positive ions. These positive ions probably originate from the coal but are of unknown identity and are readsorbed on the negative lattice sites of the coal surface. The latter possibility is diagrammed in figure 22. Hydrophilic sites on the coal surface are represented as negatively charged squares and uncharged hydrophobic sites as circles (fig. 22, upper left box). The negatively charged sites probably originate from oxidation of the organic coal matrix and from inorganic oxide impurities in the coal, particularly clays. When coal is wetted in situ during genesis, multivalent positive ions in ground water, or solubilized from the coal, are attracted to the negative sites on the coal surface to form an inner layer of positive ions on hydrophilic sites as illustrated (fig. 22, upper right box). The moisture content of the coal may determine the extent of the distribution of the positive ions on the sites. Also, development of additional negative sites through oxidation upon exposure and distribution of positive ions through an adsorbed moisture layer after exposure may occur.

When anionic surfactant is applied to the coal surface, two things can happen, one desirable and one undesirable. To achieve improved wetting of coal, it is desirable for the hydrophobic tail of the surfactant to attach itself to the hydrophobic sites on the coal surface, which orients the amphipathic surfactant molecule with it hydrophilic head toward the aqueous phase, as shown in the lower left box of figure 22. This orientation effectively converts the hydrophobic coal sites to a hydrophilic or wettable state, and the previous negatively charged hydrophilic wetting sites remain unchanged as far as ease of wettability is concerned.

However, the negative head of the anionic surfactant molecule is also capable of attaching to the positive inner layer on the coal's natural hydrophilic sites in an ion-exchange-type reaction. This ion-exchange reaction, where negative surfactant anions replace other attached anions on the positive inner layer, converts the hydrophilic sites to an undesirable nonwetting state, owing to the orientation of the attached surfactant with its hydrophobic tail directed toward the aqueous phase (fig. 22, lower right box).

In the case of exposed coal and prior adsorption of water molecules on the coal surface, it is suggested that the adsorbed water might furnish the medium by which the multivalent positive ions are transported to the hydrophilic sites. Alternatively, some sort of reversible hydrolysis
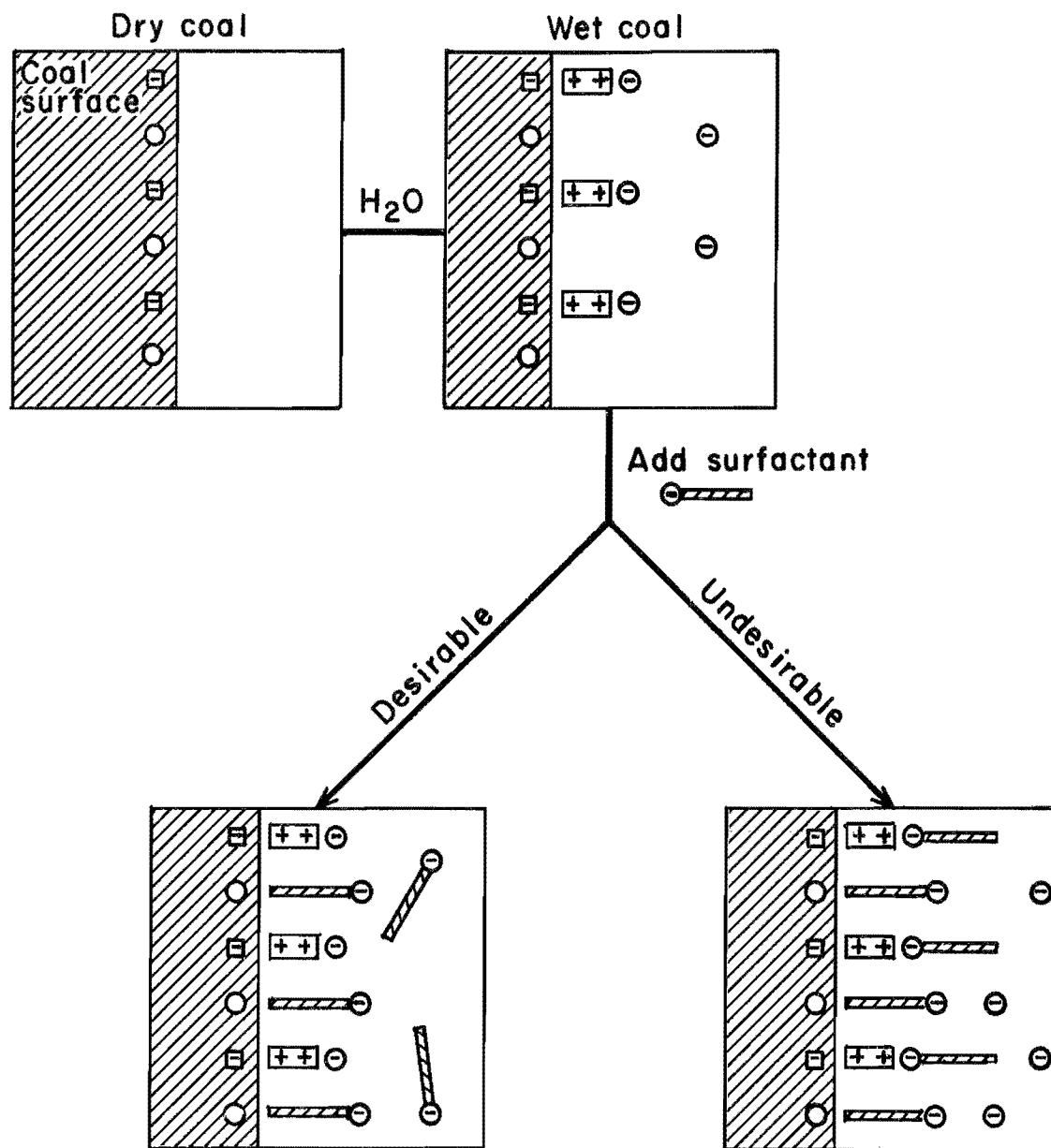
Figure 22.—Schematic of wetting model for anionic surfactants on coal illustrating manner in which auto-phobicity can occur through adverse adsorption of surfactant on positive ion layer.

reaction is occurring between functional groups on the coal surface and adsorbed water molecules to form positively charged species or adsorption sites. The mirrorlike resemblance noted earlier between the ΔW curves for pure water and anionic surfactant solution tends to support this latter speculation.

CONCLUSIONS

1. It is concluded that adsorption of moisture can significantly influence the wetting response changes occurring after exposure of coals to air. On the other hand, possible surface oxidation occurring during exposure of coal to air for 8 days or less does not appear to be a significant factor in wetting behavior.

2. Testing of the capillary wetting response for surfactant solutions on coals should be carried out on coals exposed to humidities corresponding to those expected at the site of application of the wetting agent if a true measure of the practical efficacy of the reagent is to be obtained. Also, it is recommended that comparison of surfactant wettability results be made on coal samples exposed to comparable humidities.

3. The wetting response of unexposed coals for anionic surfactants was generally superior to that for nonionic surfactants, but if a higher ranked coal was exposed to air atmosphere for several days, the wetting performance of the two surfactants was sometimes reversed. It is hypothesized that this result was caused by an adsorbed moisture layer, which represses anionic surfactant performance and promotes nonionic performance.

4. It is suggested that the improved wetting displayed by EAG nonionic surfactant on exposed coal is the result of hydrogen bonding between adsorbed water molecules on the coal surface and the ethylene oxide groups of the surfactant. For anionic surfactants, the situation is more complex. In this case, adverse surfactant orientation upon adsorption and the absence of hydrogen bonding are thought to be major factors controlling the wetting behavior.

5. There is a possibility that pore structure changes are occurring within the coal that alter the wetting characteristics after exposure for coals having inherent moisture in the 14- to 20-pct range.

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